

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-245 629

SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM
THE PETROCHEMICAL INDUSTRY
VOLUME III

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

APRIL 1974

KEEP UP TO DATE

Between the time you ordered this report—which is only one of the hundreds of thousands in the NTIS information collection available to you—and the time you are reading this message, several *new* reports relevant to your interests probably have entered the collection.

Subscribe to the **Weekly Government Abstracts** series that will bring you summaries of new reports as soon as they are received by NTIS from the originators of the research. The WGA's are an NTIS weekly newsletter service covering the most recent research findings in 25 areas of industrial, technological, and sociological interest—invaluable information for executives and professionals who must keep up to date.

The executive and professional information service provided by NTIS in the **Weekly Government Abstracts** newsletters will give you thorough and comprehensive coverage of government-conducted or sponsored re-

search activities. And you'll get this important information within two weeks of the time it's released by originating agencies.

WGA newsletters are computer produced and electronically photocomposed to slash the time gap between the release of a report and its availability. You can learn about technical innovations immediately—and use them in the most meaningful and productive ways possible for your organization. Please request NTIS-PR-205/PCW for more information.

The weekly newsletter series will keep you current. But *learn what you have missed in the past* by ordering a computer **NTISearch** of all the research reports in your area of interest, dating as far back as 1964, if you wish. Please request NTIS-PR-186/PCN for more information.

WRITE: Managing Editor
5285 Port Royal Road
Springfield, VA 22161

Keep Up To Date With SRIM

SRIM (Selected Research in Microfiche) provides you with regular, automatic distribution of the complete texts of NTIS research reports *only* in the subject areas you select. SRIM covers almost all Government research reports by subject area and/or the originating Federal or local government agency. You may subscribe by any category or subcategory of our WGA (**Weekly Government Abstracts**) or **Government Reports Announcements and Index** categories, or to the reports issued by a particular agency such as the Department of Defense, Federal Energy Administration, or Environmental Protection Agency. Other options that will give you greater selectivity are available on request.

The cost of SRIM service is only 45¢ domestic (60¢ foreign) for each complete

microfiched report. Your SRIM service begins as soon as your order is received and processed and you will receive biweekly shipments thereafter. If you wish, your service will be backdated to furnish you microfiche of reports issued earlier.

Because of contractual arrangements with several Special Technology Groups, not all NTIS reports are distributed in the SRIM program. You will receive a notice in your microfiche shipments identifying the exceptionally priced reports not available through SRIM.

A deposit account with NTIS is required before this service can be initiated. If you have specific questions concerning this service, please call (703) 451-1558, or write NTIS, attention SRIM Product Manager.

This information product distributed by

NTIS

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

PB 245 629

EPA-450/3-73/005-c

269075

APRIL 1974

**SURVEY REPORTS
ON ATMOSPHERIC EMISSIONS
FROM THE PETROCHEMICAL
INDUSTRY
VOLUME III**



**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711**

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. Department of Commerce
Springfield VA 22151

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)			
1. REPORT NO. EPA-450/3-73/005-c		3. PERFORMING ORGANIZATION REPORT NO. PB245629	
4. TITLE AND SUBTITLE Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume III		5. REPORT DATE April 1974 (date of issue)	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) J. W. Pervier, R. C. Barley, D. E. Field, B. M. Friedman R. B. Morris, and W. A. Schwartz		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Houdry Division/Air Products and Chemicals P.O. Box 427 Marcus Hook, Pennsylvania 19061		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. 68-02-0255	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Air Quality Planning & Standards Industrial Studies Branch Research Triangle Park, N.C. 27711		13. TYPE OF REPORT AND PERIOD COVERED Final Report	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry. A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in four volumes numbered EPA-450/3-73-005-a, -b, -c, and -d. This volume covers the following processes: Maleic Anhydride, Nylon 6, Nylon 66, Oxo Processes, Phenol, High-Density Polyethylene, and Low-Density Polyethylene. For each process the report includes a process description, a process emission inventory, a catalog of emission control equipment, a list of producers, and an evaluation of the significance of the air pollution from the process. Also included is a summary table of emissions to the atmosphere from all the processes studied.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Maleic Anhydride		Petrochemical Industry	7A
Carbon Monoxide		Particulates	7B
Hydrocarbons		Nylon 6	7C
Nitrogen Dioxide		Nylon 66	13B
Sulfur Dioxide		Oxo Processes	13H
Phenol		High-Density Polyethylene	
Polyethylene		Low-Density Polyethylene	
19. DISTRIBUTION STATEMENT Release Unlimited		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 259
		20. SECURITY CLASS (This page) Unclassified	22. PRICE \$8.50

**SURVEY REPORTS
ON ATMOSPHERIC EMISSIONS
FROM THE PETROCHEMICAL
INDUSTRY
VOLUME III**

by

J. W. Pervier, R. C. Barley, D. E. Field,
B. M. Friedman, R. B. Morris, W. A. Schwartz

Houdry Division
Air Products and Chemicals, Inc.
P. O. Box 427
Marcus Hook, Pennsylvania 19061

Contract No. 68-02-0255

EPA Project Officer: Leslie B. Evans

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

April 1974

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - as supplies permit - from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by Air Products and Chemicals, Inc., Marcus Hook, Pennsylvania, in fulfillment of Contract No. 68-02-0255. The contents of this report are reproduced herein as received from Air Products and Chemicals, Inc. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-73-005-c

PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry.

A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in these four volumes numbered EPA 450/3-73-005-a, -b, -c, and -d. The Tables of Contents of these reports list the processes that have been surveyed.

Those processes which have a significant impact on air quality are being studied in more detail by EPA. These in-depth studies will be published separately in a series of volumes entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a, -b, -c, etc.) At the time of this writing, a total of seven petrochemicals produced by 11 distinctly different processes has been selected for this type of study. Three of these processes, used to produce two chemicals (polyethylene and formaldehyde), were selected because the survey reports indicated further study was warranted. The other five chemicals (carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride and ethylene oxide) were selected on the basis of expert knowledge of the pollution potential of their production processes. One or more volumes in the report series will be devoted to each of these chemicals.

ACKNOWLEDGEMENTS

Survey and study work such as that described in this report have value only to the extent of the value of the input data. Without the fullest cooperation of the companies involved in producing the petrochemicals that have been studied, this report would not have been possible. Air Products wishes to acknowledge this cooperation by commending:

The U. S. Petrochemical Industry
Member Companies of the Industry
The Manufacturing Chemists Association

Table of Contents

	<u>Page Number</u>
Summary	i
Introduction	1
Discussion	2
Results	8
Conclusions	9

Survey Reports (Located by tabs)

Maleic Anhydride
Nylon 6
Nylon 6,6
Oxo Process
Phenol
High Density Polyethylene
Low Density Polyethylene

Appendicies (Located by tabs)

Appendix I - Mailing List
Appendix II - Example Questionnaire
Appendix III - Questionnaire Summary
Appendix IV - Significance of Pollution
Appendix V - Efficiency Ratings

List of Tables and Figures

<u>Table Number</u>	<u>Title</u>
I	Emissions Summary (3 pages)
II	Total Emissions, All Pollutants, by 1980*
III	Total Annual Weighted Emissions, by 1980*
IV	Significant Emission Index*
V	Number of New Plants (1973-1980)*

*Fifteen highest ranks from Table I.

NOTE: There are numerous tables and figures in the Survey Reports that are included in the appendicies of this report. These tables and figures are separately listed in each appendix.

SUMMARY

A study of air pollution as caused by the petrochemical industry has been undertaken in order to provide data that the Environmental Protection Agency can use in the fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of the study includes most petrochemicals which fall into one or more of the classifications of (a) large production, (b) high growth rate, and (c) significant air pollution. The processes for the production of each of these selected chemicals have been studied and the emissions from each tabulated on the basis of data from an Industry Questionnaire. A survey report prepared for each process provides a method for ranking the significance of the air pollution from these processes. In-depth studies on those processes which are considered to be among the more significant polluters either have been or will be provided.

To date, drafts of in-depth studies on seven processes have been submitted. In addition, two further processes have been selected for in-depth study and work on these is in progress. All of these in-depth studies will be separately reported under Report Number EPA-450/3-73-006 a, b, c, etc.

A total of 33 Survey Reports have been completed and are reported here, or in one of the other three volumes of this report series.

1. Introduction

A study has been undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study is to provide data that are necessary to support the Clean Air Amendments of 1970.

The information sought includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an industry questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

A method for rating the significance of air emissions was established and is used to rank the processes as they are studied. The goal of the ranking technique is to aid in the selection of candidates for in-depth study. These studies go beyond the types of information outlined above and include technical and economic information on "best systems" of emission reduction, the economic impact of these systems, deficiencies in petrochemical pollution control technology and potential research and development programs to overcome these deficiencies. These studies also recommend specific plants for source testing and present suggested checklists for inspectors.

This final report presents a description of the industry surveys that have been completed, as well as a status summary of work on the in-depth studies.

The Appendices of this report include each of the 33 Survey Reports that were prepared during the course of the study.

II. Discussion

A. Petrochemicals to be Studied

There are more than 200 different petrochemicals in current production in the United States. Many of these are produced by two or more processes that are substantially different both with respect to process techniques and nature of air emissions. Although it may eventually become necessary to study all of these, it is obvious that the immediate need is to study the largest tonnage, fastest growth processes that produce the most pollution.

Recognizing this immediate need, a committee of Air Products' employees and consultants reviewed the entire list of chemicals and prepared a list of thirty chemicals which were recommended for primary consideration in the study and an additional list of fourteen chemicals that should receive secondary consideration. Since this was only a qualitative evaluation it was modified slightly as additional information was received and after consultation with the Environmental Protection Agency (EPA).

The final modified list of chemicals to be studied included all but three from the original primary recommendations. In addition, four chemicals were added and one was broken into two categories (namely low and high density polyethylene) because of distinct differences in the nature of the final products. This resulted in thirty-two chemicals for study and forty one processes which are sufficiently different to warrant separate consideration. Hence, the following list of petrochemicals is the subject of this study.

Acetaldehyde (2 processes)	Nylon 6
Acetic Acid (3 processes)	Nylon 6,6
Acetic Anhydride	"Oxo" Alcohols and Aldehydes
Acrylonitrile	Phenol
Adipic Acid	Phthalic Anhydride (2 processes)
Adiponitrile (2 processes)	Polyethylene (high density)
Carbon Black	Polyethylene (low density)
Carbon Disulfide	Polypropylene
Cyclohexanone	Polystyrene
Ethylene	Polyvinyl Chloride
Ethylene Dichloride (2 processes)	Styrene
Ethylene Oxide (2 processes)	Styrene - Butadiene Rubber
Formaldehyde (2 processes)	Terephthalic Acid (1)
Glycerol	Toluene Di-isocyanate (2)
Hydrogen Cyanide	Vinyl Acetate (2 processes)
Maleic Anhydride	Vinyl Chloride

- (1) Includes dimethyl terephthalate.
- (2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

B. Preliminary Investigations

Immediately upon completion of the preliminary study lists, a literature review was begun on those chemicals which were considered likely candidates for study. The purpose of the review was to prepare an informal "Process Portfolio" for each chemical. Included in the portfolio are data concerning processes for producing the chemical, estimates of growth in production, estimates of production costs, names,

locations and published capacities of producers, approximations of overall plant material balances and any available data on emissions or their control as related to the specific process.

The fundamental purpose of these literature reviews was to obtain background knowledge to supplement what was ultimately to be learned from completed Industry Questionnaires. A second and very important purpose was to determine plant locations and names of companies producing each chemical. This information was then used to contact responsible individuals in each organization (usually by telephone) to obtain the name and address of the person to whom the Industry Questionnaire should be directed. It is believed that this approach greatly expedited the completion of questionnaires. The mailing list that was used is included as Appendix I of this report.

C. Industry Questionnaire

Soon after the initiation of the petrochemical pollution study, a draft questionnaire was submitted by Air Products to the Environmental Protection Agency. It had been decided that completion of this questionnaire by industry would provide much of the information necessary to the performance of the study. The nature and format of each question was reviewed by EPA engineers and discussed with Air Products engineers to arrive at a modified version of the originally proposed questionnaire.

The modified questionnaire was then submitted to and discussed with an Industry Advisory Committee (IAC) to obtain a final version for submission to the Office of Management and Budget (OMB) for final approval, as required prior to any U. S. Government survey of national industries. The following listed organizations, in addition to the EPA and Air Products, were represented at the IAC meeting:

Trade Associations

Industrial Gas Cleaning Institute
Manufacturing Chemists Association

Petrochemical Producers

B. F. Goodrich Chemical Company
E. I. duPont deNemours and Company
Exxon Chemical Company
FMC Corporation
Monsanto Company
Northern Petrochemical Company
Shell Chemical Company
Tenneco Chemicals, Inc.
Union Carbide Corporation

Manufacturers of Pollution Control Devices

John Zink Company
UOP Air Correction Division

State Pollution Control Departments

New Jersey
Texas

The questionnaire, along with a detailed instruction sheet and an example questionnaire (which had been completed by Air Products for a fictitious process that was "invented" for this purpose) were submitted to the CAA for approval. In due course, approval was received and OMB Approval Number 158-S-72019 was assigned to the questionnaire. Copies of the approved instruction sheet, example questionnaire are included as Appendix II of this report.

The questionnaires were mailed in accordance with the mailing list already discussed and with a cover letter that had been prepared and signed by the EPA Project Officer. The cover letter was typed in a manner that permitted the insertion of the name and address of the recipient at the top of the first page and the name of the process, the plant location and an expected return date at the bottom of the first page. A copy of this letter of transmittal is also included in Appendix II.

Understandably, because of the dynamic nature of the petrochemical industry, about 10 percent of the questionnaires were directed to plants which were no longer in operation, were still under construction, were out-of-date processes or were too small to be considered as typical. This did not present a serious problem in most cases because (a) 100 percent of the plants were not surveyed and (b) the project timing permitted a second mailing when necessary. Appendix III tabulates the number of questionnaires incorporated into each study.

One questionnaire problem that has not been resolved is confidentiality. Some respondents omitted information that they consider to be proprietary. Others followed instructions by giving the data but then marked the sheet (or questionnaire) "Confidential". The EPA is presently trying to resolve this problem, but until they do the data will be unavailable for inclusion in any Air Products' reports.

D. Screening Studies

Completed questionnaires were returned by the various respondents to the EPA's Project Officer, Mr. L. B. Evans. After reviewing them for confidentiality, he forwarded the non-confidential data to Air Products. These data form the basis for what has been named a "Survey Report". The purpose of the survey reports being to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". These reports are included as appendices to this report.

Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for calculating a Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix IV of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emissions Summary Table that constitutes part of this report. This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes being studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process (Block) flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were established for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) are proposed.
2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR are proposed.

The bases for these ratings and example calculations are included in Appendix V of this report.

E. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furance Process for producing Carbon Black.
2. The Sohio Process for producing Acrylonitrile.
3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional processes be "nominated" for in-depth study. The chemicals involved are phthalic anhydride, formaldehyde and ethylene oxide. Work on these indicated a need for four additional in-depth studies as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.
2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst.
3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.
4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

Drafts of these have been submitted to the EPA and reviewed by the Industry Advisory Committee. The phthalic anhydride report also includes a section on production from naphthalene by air oxidation, a process which is considered to be a significant polluter in today's environment but without significant growth potential.

These seven in-depth studies will be separately issued in final report form, under Report Number EPA-450/3-73-006 a, b, c, etc.

An in-depth study, besides containing all the elements of the screening studies, delves into questions such as "What are the best demonstrated systems for emission reduction?", "What is the economic impact of emission control on the industry involved?", "What deficiencies exist in sampling, analytical and control technology for the industry involved?".

In striving to obtain answers to these questions, the reports include data on the cost effectiveness of the various pollution control techniques source testing recommendations, industry growth projections, inspection procedures and checklists, model plant studies of the processes and descriptions of research and development programs that could lead to emission reductions.

Much of the information required to answer these questions came from the completed Industry Questionnaires and the Process Portfolios. However, the depth of understanding that is required in the preparation of such a document can only be obtained through direct contact with the companies that are involved in the operation of the processes being studied. Three methods for making this contact were available to Air Products. The first two are self-evident, as follows: Each questionnaire contains the name, address and telephone number of an individual who can provide additional information. By speaking with him, further insight was obtained into the pollution control problems that are specific to the process being studied; or through him, a visit to an operating plant was sometimes arranged, thus achieving a degree of first hand knowledge.

However, it was felt that these two techniques might fall short of the level of knowledge desired. Thus, a third, and unique procedure was arranged. The Manufacturing Chemists Association (MCA) set up, through

its Air Quality Committee (AQC), a Coordinating Technical Group (CTG) for each in-depth process. The role of each CTG was to:

1. Assist in the obtaining of answers to specific questions.
2. Provide a review and commentary (without veto power) on drafts of reports.

The AQC named one committee member to provide liaison. In several cases, he is also one of the industry's specialists for the process in question. If not, one other individual was named to provide CTG leadership. Coordination of CTG activities was provided by Mr. Howard Guest of Union Carbide Corporation who is also on the EPA's Industry Advisory Committee as the MCA Representative. CTG leadership is as follows:

<u>Chemical</u>	<u>AQC Member</u>	<u>Other</u>
Carbon Black	C. B. Beck Cabot Corporation	None
Acrylonitrile	W. R. Chalker Du Pont	R. E. Farrell Sohio
Formaldehyde	W. B. Barton Borden	None
Ethylene Dichloride	W. F. Bixby B. F. Goodrich	None
Phthalic Anhydride	E. P. Wheeler Monsanto	Paul Hodges Monsanto
Ethylene Oxide	H. R. Guest Union Carbide	H. D. Coombs Union Carbide

F. Current Status

Survey Reports on each of the 33 processes that were selected for this type of study have been completed, following review of the drafts by both the EPA and the Petrochemical Industry. These reports constitute the subject matter of this report.

In-depth studies of the seven processes mentioned above have been completed in draft form, submitted to the EPA for initial review, discussed in a public meeting with the Industry Advisory Committee and re-submitted to the EPA in revised form. They are currently receiving final EPA review and will be issued as final reports, following that review.

The EPA has now selected two additional processes for in-depth study and work on these is currently in progress. They are:

1. High Density Polyethylene via the Low and Intermediate Pressure Polymerization of Ethylene.
2. Low Density Polyethylene via the High Pressure Polymerization of Ethylene.

III. Results

The nature of this project is such that it is not possible to report any "results" in accordance with the usual meaning of the word. Obviously, the results are the Survey Reports and In-Depth Studies that have been prepared. However, a tabulation of the emission data collected in the study and summarized in each of these reports will be useful to the EPA in the selection of those processes which will be either studied in-depth at some future date, or selected for the preparation of new source standards. Such a tabulation, entitled "Emissions Summary Table", is attached.

IV. Conclusions

As was stated above under "Results", the conclusions reached are specific to each study and, hence, are given in the individual reports. Ultimately, some conclusions are reachable relative to decisions on processes which require future in-depth studies or processes which warrant the promulgation of new source standards.

A firm basis for selecting these processes is difficult to achieve, but the data contained in the Emissions Summary Table can be of value in setting a basis, or selecting processes.

It is imperative, when using the table, to be aware of the following facts.

1. The data for some processes are based on 100 percent survey of the industry, while others are based on less than 100 percent with some as few as a single questionnaire.
2. Some of the reported data are based on stack sampling, others on continuous monitoring and still others on the "best estimate" by the person responsible for the questionnaire.
3. Air Products attempted to use sound engineering judgement in obtaining emission factors, industry capacities and growth projections. However, other engineering firms, using the same degree of diligence would undoubtedly arrive at somewhat different final values.

Thus, the tabulation should be used as a guide but not as a rigorous comparison of process emissions.

Furthermore, data on toxicity of emissions, odors and persistence of emitted compounds are not included in the tabulation. In addition, great care must be used when evaluating the weighted emission rates because of the wide range in noxiousness of the materials lumped together in the two most heavily weighted categories. For example, "hydrocarbons" includes both ethane and formaldehyde and "particulates" includes both phthalic anhydride and the permanent hardness of incinerated water.

Bearing all of these qualifications in mind, several "top 15" rankings of processes can be made, as in Tables II through V. Obviously, one of these tables could be used to select the more significant polluters directly. Of course, other rankings could be made, such as leading emitters of NO_x or particulates, etc. Using these four tables, however, one analysis might be that the number of times a process appears in these tables is a measure of its pollution significance, or in summary:

Appear in 4 Tables

Carbon Black
Low Density Polyethylene
High Density Polyethylene
Cyclohexanone
Polypropylene
Polyvinyl Chloride
Ethylene Oxide

Appear in 3 Tables

Acrylonitrile
Adiponitrile (Butadiene)
Ethylene Dichloride (Oxychlorination)
Dimethyl Terephthalate
Ethylene Dichloride (Direct)
Ethylene

Appear in 2 Tables

Maleic Anhydride
Isocyanates
Phenol
Formaldehyde (Silver)

Appear in 1 Table

Phthalic Anhydride
Formaldehyde (Iron Oxide)
Polystyrene
Nylon 6
Nylon 6,6
Vinyl Chloride

Thus, on this basis and in retrospect, it could be concluded that four of the selected in-depth studies (carbon black, ethylene oxide, and both low and high density polyethylene) were justified but that three of them (phthalic anhydride and both formaldehyde processes) were of lesser importance.

On the same basis, seven processes should be considered for future in-depth studies, namely:

Cyclohexanone
Polypropylene
Polyvinyl Chloride
Adiponitrile (Butadiene Process)
Dimethyl Terephthalate (and TPA)
Ethylene Dichloride (Direct)
Ethylene

Obviously, many alternative bases could be established. It is not the function of this report to select a basis for initiating future studies because the priorities of the EPA are unknown. The most apparent of these bases are the ones suggested by Tables II through V, namely the worst total polluters, the worst polluters on a weighted basis, the greatest increase in pollution (total or weighted) or the largest numbers of new plants. In addition, noxiousness of the emissions (photo-chemical reactivity, toxicity, odor, persistence) could be considered in making a selection.

TABLE 1
EMISSIONS SUMMARY

Page 1 of 3

ESTIMATED (1) CURRENT AIR EMISSIONS, MT TSP/YEAR						
Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene via Ethanol	1.1	0	0	0	1.1	86
Acetic Acid via Methanol	0	0	0	27	27	27
via Butane	40	0	0	0	40	1
via Acetaldehyde	6.1	0	0	14	54	3,215
Acetic Anhydride via Acetic Acid	3.1	0	0	1.3	7.4	490
Acrylonitrile (9)	183	5.5	0	5.5	8.6	253
Adipic Acid	0	29.6	0	196	385	15,000
Adiponitrile via Butadiene	11.2	50.5	0	0.14	30	1,190
via Adipic Acid	0	0.04	0	0	66.4	3,200
Carbon Black	156	8.1	21.6	0	4,060	17,544
Carbon Disulfide	0.15	0.3	4.5	0	5.1	120
Cyclohexanone	70	0	0	77.5	148	5,700
Dimethyl Terephthalate (STPA)	91	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxichlorination	95.1	0.4	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0.41	0	0	0.91	56
Isocyanates	1.3	0	0.02	86	88	231
Maleic Anhydride	34	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	5.5	330
Oxo Process	5.75	0.01	0	19.5	24.8	440
Phenol	24.3	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	51.7	422
via Naphthalene	0	1.9	0	45	47	160
High Density Polyethylene	79	2.3	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	37.6	2,950
Polystyrene	20	0.4	0	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	5.3	425
via Ethylene	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100 surveys. All based on engineering judgement of best current control. Probably has up to 10% low bias.

(2) Assumes future plants will employ best current control techniques.

(3) Excludes methane, includes HPS and all volatile organics.

(4) Includes non-volatile organics and inorganics.

(5) Weighting factors used are: hydrocarbons - 60, SO_x - 40, SO_2 - 20, and CO - 1.

(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".

(7) Totals are not equal across and down due to rounding.

(8) Emissions based on what is now an obsolete catalyst. See Report No. EPA-550/3-73-006 for up-to-date information.

TABLE 1
EMISSION SUMMARY

Page 2 of 3

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulate (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
Acetic Acid via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
Acetic Acid via Ethanol	0	0	0	0	0	0	0
Acetic Anhydride via Acetic Acid	12.2	0	0	0	2.5	14.7	980
Acrylonitrile (9)	0.73	0	0	0	1.42	2.15	60
Adipic Acid	284	0	8.5	0	304	596	23,000
Adiponitrile via Butadiene	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Adipic Acid	10.5	4.4	47.5	0	62.4	62.4	3,010
Carbon Black	64	0.5	0.04	0	0	0.54	30
Carbon Disulfide	0.04	3.3	2.8	8.9	1,590	1,670	7,200
Cyclohexanone	77.2	0.07	0.03	1.1	0	1.24	30
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	85.1	162	6,260
Ethylene	14.8	0.2	0.2	61.5	0.2	77	6,040
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	2,430
Ethylene Oxide	34.2	0	0	0	34.2	34.2	8,800
Formaldehyde via Silver Catalyst	32.8	0	0.15	0.05	0	33	2,740
Formaldehyde via Iron Oxide Catalyst	14.8	0	0	0	81.5	81.5	2,650
Glycerol via Epichlorohydrin	17.6	0	0	0	17.0	34.6	1,250
Hydrogen Cyanide Direct Process	8.9	0	0	0	0	8.9	1,445
Isocyanates	0	0	0	0	0	0	700
Maleic Anhydride	1.2	0.7	0	0.02	85	87	225
Nylon 6	31	0	0	0	241	272	2,720
Nylon 6,6	0	3.2	0	0	0	3.2	194
Oxo Process	3.86	5.3	0	0	0	5.3	318
Phenol	21.3	0.01	0.05	0	14.3	18.2	325
Phthalic Anhydride via (n-Xylene	0.3	13.2	0.8	6.8	113	134	1,704
Phthalic Anhydride via Naphthalene	0	0	0	0	0	0	1,100
High Density Polyethylene	210	6.2	0	0	216	216	17,200
Low Density Polyethylene	262	5	0	0	267	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	21.47	21.47	1,640
Polyvinyl Chloride	53	10	0	0	63	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
Vinyl Chloride via Ethylene	0	0	TR	0	0	TR	TR
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

- (1) In most instances numbers are based on less than 100 surveys. All based on engineering judgement of best current control. Probably has up to 10% low bias.
- (2) Assumes future plants will employ best current control techniques.
- (3) Excludes methane, includes H₂S and all volatile organics.
- (4) Includes non-volatile organics and inorganics.
- (5) Weighting factors used are: hydrocarbons = 60, NO_x = 40, SO_x = 40, and CO = 1.
- (6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
- (7) Totals are not equal across and down due to rounding.
- (8) See sheet 1 of 3.

TABLE 1
EMISSIONS SUMMARY

Page 3 of 3

	Emissions (2), Mm lbs./year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity Mm lbs./year	
	Total by 1980	Total Weighted (%) by 1980		Current	by 1980
Acetaldehyde via Ethylene	2.3	182	0	1,100	2,440
via Ethanol	27	27	0	900	900
Acetic Acid via Methanol	0.08	3	4	500	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,445	3,200 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	873	1,100
Cyclohexanone	310	11,940	10	1,800	3,600
Dimethyl Terephthalate (vTPA)	265	13,500	8	2,865	5,900
Ethylene	96	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,414	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	455	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via o-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,249	21,100
Polypropylene	190	15,160	32	1,100	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	376
via Ethylene	78	18	4	1,280	2,200
Vinyl Chloride	45	3,430	10	5,400	13,000
Totals	10,605 (7)	264,420 (7)			

- (1) In most instances numbers are based on less than 100 surveys. All based on engineering judgment of best current control. Probably has up to 10 low bias.
- (2) Assumes future plants will employ best current control techniques.
- (3) Excludes methane, includes H₂S and all volatile organics.
- (4) Includes non-volatile organics and inorganics.
- (5) Weighting factors used are: hydrocarbon = 80, particulates = 60, SO₂ = 40, SO_x = 20, and CO = 1.
- (6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
- (7) Totals are not equal across and down due to rounding.
- (8) By 1985.
- (9) See sheet 1 of 3.
- (10) Due to anticipated future shut down of marginal plants.

TABLE II

TOTAL ANNUAL EMISSIONS, ALL "POLLUTANTS", BY 1980 (MM LBS./YR.)*

Carbon Black	5,730
Acrylonitrile	980
Maleic Anhydride	566
Low Density Polyethylene	343
Cyclohexanone	310
High Density Polyethylene	297
Dimethyl Terephthalate	265
Ethylene Dichloride	253
Phthalic Anhydride (Total)	233
Formaldehyde (Silver)	212
Polypropylene	190
Isocyanates	175
Polyvinyl Chloride	137
Adiponitrile (Butadiene Process)	129
Ethylene Oxide	120

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE III

TOTAL ANNUAL WEIGHTED EMISSIONS BY 1980 (MM LBS./YR.)*

Acrylonitrile	38,000
Low Density Polyethylene	27,400
Carbon Black	24,740
High Density Polyethylene	23,600
Ethylene Dichloride (Oxychlorination)	16,450
Polypropylene	15,140
Dimethyl Terephthalate	13,500
Cyclohexanone	11,960
Polyvinyl Chloride	10,540
Ethylene Oxide	9,530
Adiponitrile (Butadiene Process)	6,210
Maleic Anhydride	5,670
Ethylene Dichloride (Direct)	5,040
Ethylene	3,670
Phenol	3,640

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE IV

SIGNIFICANT EMISSION INDEX*

Acrylonitrile	23,000
Low Density Polyethylene	21,300
High Density Polyethylene	17,200
Polypropylene	12,190
Ethylene Dichloride (Oxychlorination)	8,800
Carbon Black	7,200
Cyclohexanone	6,260
Dimethyl Terephthalate	6,040
Polyvinyl Chloride	4,840
Adiponitrile (Butadiene)	3,010
Ethylene Dichloride (Direct)	2,740
Maleic Anhydride	2,720
Ethylene Oxide	2,650
Ethylene	2,430
Vinyl Chloride	2,170

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE V

NUMBER OF NEW PLANTS (1973-1980)*

Low Density Polyethylene	41
Formaldehyde (Silver)	40
Polypropylene	32
High Density Polyethylene	31
Polyvinyl Chloride	25
Polystyrene	23
Ethylene	21
Ethylene Oxide	15
Carbon Black	13
Formaldehyde (Iron Oxide)	12
Phenol	11
Cyclohexanone	10
Isocyanates	10
Nylon 6	10
Nylon 6,6	10
Ethylene Dichloride (Direct)	10

*Fifteen highest numbers, as summarized in Table I, for this category.

Maleic Anhydride

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	MA-1
II. Process Description	MA-2
III. Plant Emissions	MA-3
IV. Emission Control	MA-5
V. Significance of Pollution	MA-7
VI. Maleic Anhydride Producers	MA-8

List of Illustrations and Tables

Flow Diagram	Figure MA-I
Net Material Balance	Table MA-I
Gross Heat Balance	Table MA-II
National Emissions Inventory	Table MA-III
Catalog of Emission Control Devices	Table MA-IV
Number of New Plants by 1980	Table MA-V
Emission Source Summary	Table MA-VI
Weighted Emission Rates	Table MA-VII

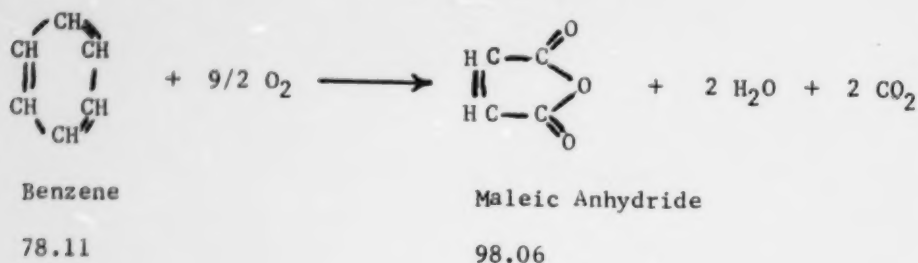
I. Introduction

Maleic Anhydride is a white crystalline solid that is normally marketed in tablet form although some producers have a substantial bulk market in tank cars or wagons. Its major use, accounting for about 50% of total production, is in the formulation of polyester resins. Additionally, it is an intermediate in the production of fumaric acid and agricultural pesticides. Alkyd resins and other miscellaneous uses account for the remaining 25% of production.

With one exception, all U. S. maleic anhydride (direct) production is based on the vapor phase oxidation of benzene, as licensed by Scientific Design. Petro-tex, however, utilizes a feedstock of mixed butylene at their Houston plant. Lower yields and higher investment costs apparently tend to off-set the economic advantage offered by the cheaper C₄ charge material. Also, minor quantities of maleic anhydride are produced as a by-product with phthalic anhydride when the naphthalene based process is used.

II. Process Description

Benzene in the presence of a suitable catalyst may be oxidized to maleic anhydride. The primary overall reaction is:



Standard commercial practice is to conduct the reaction in the vapor phase, utilizing a V_2O_5 based catalyst.

Benzene is either carbureted with air and preheated or vaporized and then mixed with an excess of preheated air prior to being admitted to a multi-tubular catalytic reactor. The vapors pass downward (or upward in some cases) through the tubes, which contain a pelleted V_2O_5 catalyst, and exit the reactor at a temperature in the range of 750 to 850° F. The very large heat of reaction (up to 2,600 BTU/lb. of MAN) is removed by the heat of transfer fluid - molten salt or boiling mercury - that circulates around the outside of the tubes, and by air preheat.

The effluent vapors, consisting of maleic anhydride, maleic acid, carbon oxides, water and benzene, are cooled and then passed through a partial condenser and separator, where the bulk of the maleic anhydride is separated from the non-condensibles. The overhead material from the separator still contains some maleic anhydride, this material is recovered thru absorption in aqueous (or non-aqueous) solvents and recovered as maleic acid.

The crude maleic acid is converted to the anhydride by dehydration, usually by azeotropic distillation. This material is combined with the maleic anhydride recovered from the partial condenser and purified by vacuum and/or azeotropic distillation. The product is then either tableted or flaked and packaged or marketed in bulk.

The above described processing scheme is consistent with the presented flow diagram, Figure I (which see), and typical of the methods used by domestic producers. However, the reader should be cognizant of the fact that a wide variety of product recovery and purification techniques exist within the industry today.

III. Plant Emissions

A. Continuous Air Emissions

1. Product Recovery Condenser Vent (Scrubber Exhaust)

This stream is the only source of emissions reported by four of the seven respondents. Thus, it seems reasonable to categorize it as the single most important emission source for the subject process. The two main components, of a polluting nature, are carbon monoxide and benzene. The concentration of carbon monoxide varies from .87 lbs. CO/lb. of MAN to .44 lbs./lb, while the concentration of benzene varies from .20 lbs. benzene/lb. of MAN to .06 lbs./lb. As mentioned in the process description section of this report, the vapors from the condenser are vented to a scrubber for recovery of uncondensed maleic anhydride, prior to venting the effluent gases to the atmosphere. Many plants route streams from other sections of the unit to this same scrubber in order to minimize emissions and affect economy of operation through the utilization of a single large scrubber rather than several smaller ones. Unfortunately, lack of data preclude calculation of scrubber efficiency. A summary of emissions from this source are listed in Table III.

2. Product Flaking, Pelletizing, Packaging and Storage

Three respondents report emissions from this type of operation. Respondent 18-2 reports emitting .0002 lbs./lb. of maleic anhydride from his pelletizing and packaging operation. Respondent 18-6 reports 'losing' 0.6 lbs./hr. of maleic anhydride from his product storage area, however, a scrubbing device removes all of that material from the vent stream before atmospheric discharge. Respondent 18-7 also reports emissions from the subject area, again he states water scrubbing results in the complete removal of pollutants from the vent.

3. Aqueous Waste Incinerator Flue Gas

Only respondent 18-2 has reported an emission from this source. It results from the incineration of various plant generated aqueous waste streams. The respondent indicates that the only pollutants discharged as a result of this operation are .0001 lbs. of particulates (Na_2CO_3)/lb. of product.

4. Distillation and Dehydration Section Vent

Only respondent 18-2 reports emissions from this source. This is so because most other operators direct the light ends resulting from these operations to the main scrubber (see Section III-A-1). Emissions reported consist of .0001 lbs./lb. of maleic anhydride plus varying quantities of non-polluting gases. The emission is summarized in Table III.

B. Intermittent Air Emissions

No intermittent air emissions were reported.

C. Continuous Liquid Wastes

The following data relating to waste liquid production and disposal were reported by the respondents:

<u>Plant</u>	<u>Type of Waste Liquid</u>	<u>Amount MM Gal./Yr.</u>	<u>Treatment and/or Disposal Method</u>
18-1	Still washing	0.9	Outside contractor
18-2		6.3	Biological treatment
18-3		32.8	Lime neutralization
18-4		34.0	
18-5	Process water	15.5	
	Cooling tower water	17.3	
18-6	Total water outfall	110.5	To municipal sewer
18-7	Purification system wash water	3.6	To municipal sewer

D. Solid Wastes

Only three of the seven respondents reported the generation of solid waste materials. The only type of solid waste reported by the three was spent catalyst. The amounts and disposal method are reported below:

<u>Plant</u>	<u>Tons of Catalyst/Yr.</u>	<u>Disposal Method</u>
18-3	18	Landfill
18-5	30	Reprocessed
18-6	53	Landfill

E. Fugitive Emissions

None of the respondents have offered a quantitative estimate of fugitive emissions. Aside from the normal sources, such as leaking pump seals, packing gland, etc., there are two (probable) principal sources for emissions of this type in most maleic anhydride plants. They are:

- (1) Storage tank vents - very few of the respondents indicate the use of conservation vents on storage tanks. Since benzene is relatively volatile, it is reasonable to assume that moderate amounts of that material at least is 'lost' to the atmosphere.
- (2) Packaging, pelleting and flaking - most plants employing this type of solids handling equipment suffer at least some losses. It seems reasonable to assume, therefore, that these areas would represent emission sources.

F. Odors

In general, the respondents indicate that maleic anhydride is not the cause of a significant odor problem. Only one respondent reported receiving a community odor complaint in the past 12 months. Maleic anhydride was identified as the source of odor in that instance. No other respondents reported the detection of odors off the plant site.

IV. Emission Control

The various emission control devices that have been reported as being utilized by operators of maleic anhydride plants are summarized in Table IV of this report, which is entitled 'Catalog of Emission Control Devices'. The control devices may be divided into two broad categories; (1) Combustion Devices - those devices which depend on thermal (or catalytic) oxidation of combustibles for emission control, and (2) Non-Combustion Devices - devices that do not depend on combustion for emission control. In Table IV, all devices are assigned efficiency ratings (when data permits). Efficiencies are defined in terms of:

- (1) "CCR" - Completeness of Combustion Rating

$$CCR = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

- (2) "SE" - Specific Efficiency

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

- (3) "SERR" - Significance of Emission Reduction Rating

$$SERR = \frac{(\text{pollutant} \times \text{weighting factor})_{in} - (\text{pollutant} \times \text{weighting factor})_{out}}{(\text{pollutant} \times \text{weighting factor})_{in}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Combustion devices are normally assigned a CCR and a SERR rating whereas non-combustion devices are assigned SE and SERR ratings. Unfortunately none of the respondents provided sufficient data to calculate the above indicated efficiencies. Therefore, only a few general observations about the expected device performance can be made.

Scrubbers

Most plants scrub the uncondensed portion of the reactor effluent after it passes through the partial condensor. This is done principally to recover maleic anhydride. Many plants utilize this same device to scrub vent gases from various areas of the plant. However, CO and hydrocarbon emissions from this device are quite high. Appreciably better control would be achieved by coupling the product scrubber with a combustion type device. One plant (18-4) plans such an installation. They state total costs will be \$1,000,000.

Plant 18-2 and 18-7 utilize separate scrubbers to control the emissions of MAN particles from their flaking, tableting packaging operations. One would expect scrubbing efficiencies to be quite high for this service - 98%+.

Incinerators

Only one plant employs an incineration device - plant 18-2. It is used to dispose of aqueous wastes. The respondent shows no hydrocarbons, CO or other pollutants in the incinerator flue gas. However, this does not

the device performs with 100 efficiency because incinerator effluents are difficult to sample or monitor. Considering that there are no sulfur, nitrogen or halogen bearing compounds used in the process, a high SERR rating is to be expected.

Developmental work directed toward reduction in emissions for the subject process falls into the following general areas, as has been suggested by questionnaire respondents and general literature.

- (1) Substitution of oxygen for air; as the oxidizing agent.
- (2) Development of fluid bed process to permit reduction of air/benzene feed ratio.
- (3) Development of more selective catalyst.
- (4) More efficient design and better utilization of pollution control devices currently being used.
- (5) Investigate use of recycle air to improve yield and reduce emissions.

This list is by no means intended to be exhaustive, nor is knowledge available as to whether or not some of these types of work are in progress.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. The predicted growth and emission rates are both moderate. Therefore, the resultant SEI is less than for other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V and VI.

Published support for the annual growth rate upon which the Table V forecast of new plants is based may be found in the April 3, 1973 issue of Chemical Marketing, Chemical Profiles section.

On a weighted emission basis a Significant Emission Index of 2,721 has been calculated in Table VI. Thus, this number, in part, is the basis for recommending the exclusion of this process from the in-depth portion of the overall petrochemical industry study that is scheduled for the near future.

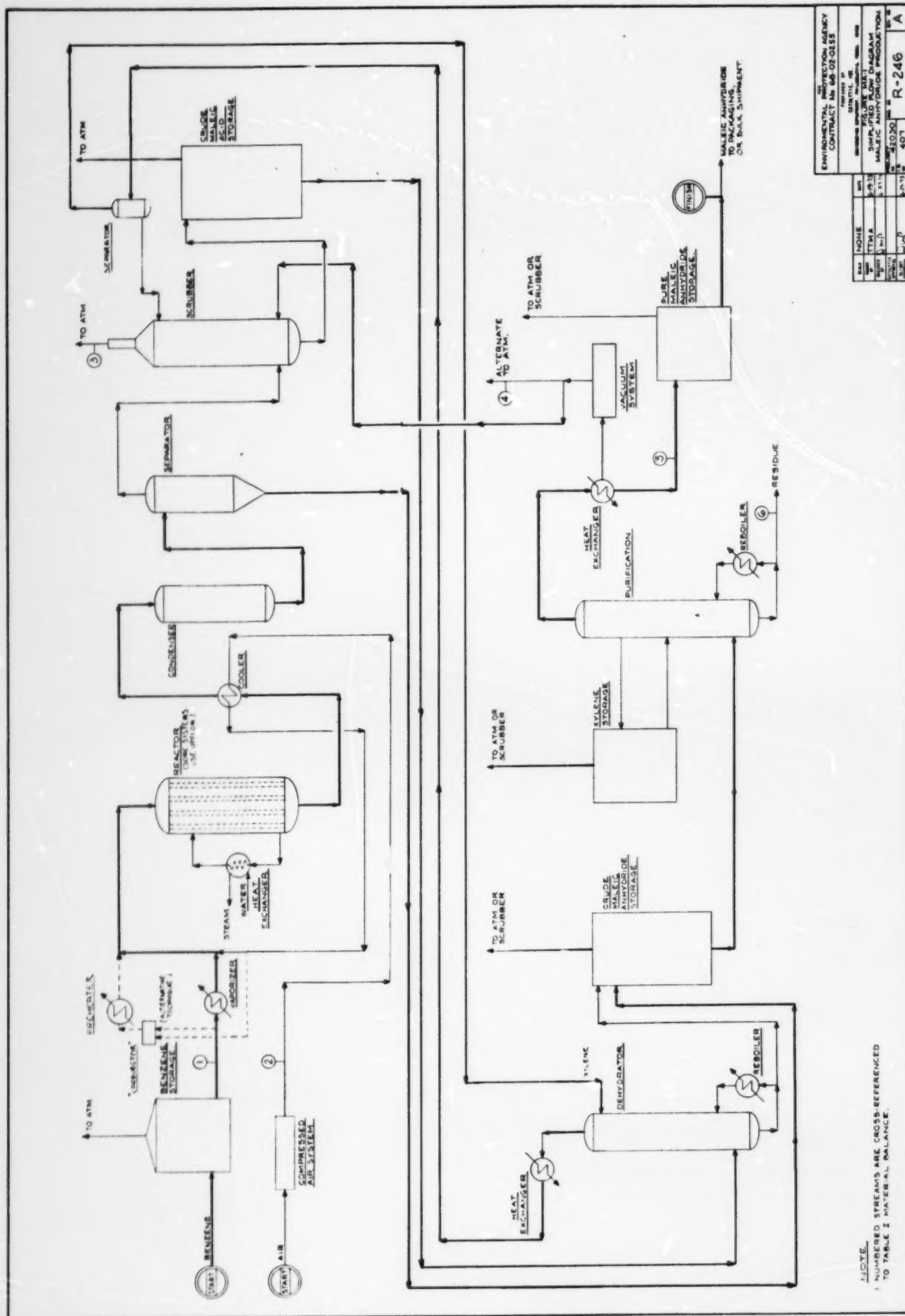
VI. Maleic Anhydride Producers

The following list shows the production capacity of the maleic anhydride producers and their location by plant.

<u>Name</u>	<u>Location</u>	<u>Capacity - MM Lbs./Year</u>
Allied Chemical Corp.	Moundsville, W. Va.	20
Koppers Company	Bridgeville Pa.	34
Monsanto Company	St. Louis, Mo.	105
Petro-tex Chemical Corp.	Houston, Texas	50
Reichhold Chemical	Elizabeth, N. J.	30
	Morris, Ill.	60
Tenneco Chemical	Fords, N. J.	20
USS Chemical Division	Pittsburgh, Pa.	<u>40</u>

Total - 359*

*1973 capacity is estimated to be 9% higher than 1972 capacity, i.e.,
1.09 x 359 = 391 MM lbs./year.



NOTE:
1. NUMBERED STREAMS ARE CROSS-REFERENCED
TO TABLE 1 MATERIAL BALANCE.

ENVIRONMENTAL PROTECTION AGENCY		CONTRACT NO. 68-02-0155	
PROJECT NO. 68-02-0155		SUBJECT: MALEIC ANHYDRIDE PRODUCTION	
DATE: 10/1/68		BY: J. R. 407	
REVISION: 1		R-246	
APPROVED: J. R. 407		A	

TABLE MA-1
MALEIC ANHYDRIDE UNIT
NET MATERIAL BALANCE - T/T

Stream I. D. No.	1	2	3	4	5	6
Component	Fresh Feed	Air	Scrubber Vent Gas	Vacuum Light Ends (1)	Product Maleic Anhydride	Refiner Heavy Ends
CO			0.303			
CO ₂			1.189			
O ₂		9.152	7.082			
N ₂		30.124	30.124			
Benzene	1.331		0.067			
Maleic Anhydride					1.000	
H ₂ O			1.644 (2)			
Misc. HC's				0.133 (3)		0.066 (3)
	1.331	39.276	40.409	0.133	1.000	0.066

(1) In some units this stream is recycled to reactor.

(2) Includes 1.001 T/T of water lost from water scrubber. If other scrubbing medium such as dibutyl phthalate is employed, water in vent is reduced to 0.553 T/T.

(3) Arbitrary split, contains oxygenated compounds rejected in waste water streams.

TABLE MA-II
MALEIC ANHYDRIDE
EX
BENZENE
CROSS REACTOR HEAT BALANCE

<u>HEAT IN</u>	<u>BTU/LB. OF MAN</u>
Benzene vaporizer and superheater	250
Exothermic heat of reaction	<u>18,000</u>
Total -	18,250
 <u>HEAT OUT</u>	
Reactor heat loss	25
Reactor temperature control	10,725
Differential enthalpy*	<u>7,500</u>
Total -	18,250

*Enthalpy Effluent - Enthalpy Feed

TABLE MA-III
NATIONAL EMISSIONS INVENTORY
MALEIC ANHYDRIDE PRODUCTION

Page 1 of 3

EPA Code Number		18-1	18-2	18-2	18-2
Date on stream		20,000	22,000	22,000	22,000
Capacity - Tons Maleic Anhydride (MAN)/yr.		0	0	0	0
Average Production - Tons MAN/yr.		0	0	0	0
Range in Production - % of Max.		0	0	0	0
Emissions to Atmosphere		0	0	0	0
Stream		0	0	0	0
Flow - SCFM		42,000	43,100	43,100	43,100
Flow Characteristic - Continuous or Intermittent		Continuous	Continuous	Continuous	Continuous
If Intermittent - Hrs /yr. of Flow		0	0	0	0
Composition - Tons/Ton of MAN		0	0	0	0
Particulate		6 1280	5.6727	0 0030	0 0001 (Nap CO ₂)
O ₂		26 3280	26.7818	0 0100	0 1091
N ₂		1.8416	1.2800	0 0009	1.8000
CO ₂		0.8674	0.6109	0 0001	0 3727
CO		2.2354	0.8727	0 0002	2 4764
H ₂ O		0 0040	0.0027	0 0001	0 0001
MAN (a)		0 0624	0.0033	0 0001	0 0001
Maleic Acid		0 0154	0.0033	0 0001	0 0001
Benzene		0 0012	0.0033	0 0001	0 0001
Formaldehyde		0 0012	0.0033	0 0001	0 0001
Formic Acid		0 0012	0.0033	0 0001	0 0001
Xylene		0 0012	0.0033	0 0001	0 0001
Sample Tap Location		0 0012	0.0033	0 0001	0 0001
Date or Frequency of Sampling		0 0012	0.0033	0 0001	0 0001
Type of Analysis		0 0012	0.0033	0 0001	0 0001
Odor Problems		0 0012	0.0033	0 0001	0 0001
Vent Stacks		0 0012	0.0033	0 0001	0 0001
Flow - SCFM per stack		21 000	43,100	16	7 400
Number		2	1	1	1
Height - Feet		79 and 99	90	85	34
Diameter - Inches		24	42	2	14
Exit Gas Temperature - °F		104	100	80	200
Emission Control Device		Water Scrubber	Water Scrubber	Water Scrubber	Water Scrubber
Type		Water Scrubber	Water Scrubber	Water Scrubber	Water Scrubber
Catalog I. D. Number		0 0870	0 0062	0 0062	0 0062
Total Hydrocarbon Emissions - Ton/Ton of MAN		0	0 0001	0 0001	0 0001
Total Particulate/Aerosol Emissions - Ton/Ton of MAN		0	0 0001	0 0001	0 0001
Total SO _x Emissions		0	0 0001	0 0001	0 0001
Total SO ₂ Emissions		0	0 0001	0 0001	0 0001
Total CO Emissions		0	0 0001	0 0001	0 0001
Benzene and Product Recovery Vent		0	0	0	0
Benzene Recovery Vent		0	0	0	0
Vacuum System Vent		0	0	0	0
Scrubber Vent		0	0	0	0
Incinerator Vent		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0	0	0
Top of Stack		0	0	0	0
Design Calc		0	0	0	0
No		0	0		

TABLE MA-III
NATIONAL EMISSIONS INVENTORY
MALEIC ANHYDRIDE PRODUCTION

EPA Code Number	18-3	18-4	18-5
Date on stream	1961		
Capacity - Tons Maleic Anhydride (MAN)/yr.	10,000	17,000	25,000
Average Production - Tons MAN/Yr.			
Range in Production - % of Max.	0	0	0
Emissions to Atmosphere			
Stream	Scrubber Vent	Scrubber Vent	Scrubber Vent
Flow - SCFM	17,000	30,000	42,000
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. of Flow			
Composition - Tons/Ton of MAN			
Particulate			
O ₂	6.9296		4.9580
N ₂	22.8232	332 1810	24 2656
CO ₂	0.8480		1 3126
CO	0.6864	0.6706	0.4434
H ₂ O	0.3928	1.5139	1.3642
MAN (a)	0.0020	0.0059	
Maleic Acid			0.0115
Benzene	0.1008	0.0616	0.0627
Formaldehyde			Incl. with
Formic Acid			Maleic Acid
Xylene	0.0116		
Sample Tap Location	Scrubber	Not Sampled	Not Specified
Date or Frequency of Sampling	Four since 1968		Infrequent
Type of Analysis	Gravimetric - Wet Chemical	Mat. Balance	Not Specified
Odor Problems	No	No	Yes
Vent Stacks			
Flow - SCFM per stack	17,000	30,000	42,000
Number	1	1	1
Height - Feet	72	24	65
Diameter - Inches	24	24	36
Exit Gas Temperature - °F	65	100	100
Emission Control Device			
Type	Water Scrubber	Water Scrubber	Water Scrubber
Catalog I. D. Number			
Total Hydrocarbon Emissions - Ton/Ton of MAN	0.1144	0.0675	0.0742
Total Particulate/Aerosol Emissions - Ton/Ton MAN	0	0	0
Total NO _x Emissions			
Total SO _x Emissions			
Total CO _x Emissions	0.6844	0.6706	0.4434

TABLE IV-III
NATIONAL EMISSIONS INVENTORY
MALEIC ANHYDRIDE PRODUCTION

EPA Code Number		18-6		18-7		18-8	
Date on stream		52,500		15,000		7,000	
Capacity - Tons Maleic Anhydride (MAN)/Yr.		0		0		Continuous	
Average Production - Tons MAN/Yr.		0		0		0	
Range in Production - % of Max.		0		0		0	
Emissions to Atmosphere		0		0		0	
Stream		Scrubber Vent		Fume Scrubber Vent		Product Recovery Vent	
Flow - SCFM		76,000		45		20,000	
Flow Characteristic - Continuous or Intermittent		Continuous		Continuous		Continuous	
if Intermittent - Hrs./Yr. of Flow							
Composition - Tons/Ton of MAN							
Particulate		3.9896		0.0015		2.4567	
O ₂		19.7250				19.0421	
N ₂		1.0363				1.0776	
CO ₂		0.4703				0.6859	
CO		1.2219				0.6521	
H ₂ O		0.0047					
MAN (a)							
Maleic Acid		0.0879		0.0015		0.1976	
Benzene		Incl. with					
Formaldehyde		MAN					
Formic Acid							
Xylene							
Sample Tap Location		Not Sampled		Not Sampled		Not Sampled	
Date or Frequency of Sampling		Not Sampled		Not Sampled		Not Sampled	
Type of Analysis		Not Sampled		Not Sampled		Not Sampled	
odor Problems		Not Sampled		Not Sampled		Not Sampled	
Vent Stacks		Not Sampled		Not Sampled		Not Sampled	
Flow - SCFM per stack		Not Specified		Not Specified		Not Specified	
Number		Not Specified		Not Specified		Not Specified	
Height - Feet		Not Specified		Not Specified		Not Specified	
Diameter - Inches		Not Specified		Not Specified		Not Specified	
Exit Gas Temperature - or		140		100		104	
Emission Control Device		Water Scrubber		Venturi Scrubber		Water Scrubber	
Type							
Catalog I. D. Number		0.0926		0.1976		0.1976	
Total Hydrocarbon Emissions - Ton/Ton of MAN		0		0		0	
Total Particulate/Aerosol Emissions - Ton/Ton MAN		0		0		0	
Total NO _x Emissions		0		0		0	
Total SO _x Emissions		0		0		0	
Total CO Emissions		0.4703		0.4703		0.4703	

TABLE MA-11
CATALOG OF EMISSION CONTROL DEVICES
MALEIC ANHYDRIDE VIA
THE OXIDATION OF XENYLENE

Page 3 of 3

WATER SOURCES		MAN-1		MAN-2		MAN-3		MAN-4	
Flow Rate	Stream I, D.	18-1	18-2	18-2	18-2	18-2	18-2	18-3	18-3
Device I, D. No.		Maleic Anhydride	Maleic Anhydride	Maleic Anhydride	Maleic Anhydride	Maleic Anhydride	Maleic Anhydride	Maleic Anhydride	Maleic Anhydride
EPA Code Number of plant		Not Specified	Not Specified	Not Specified	Not Specified	Not Specified	Not Specified	Not Specified	Not Specified
Purpose - Control Emission of									
Type - Spray									
Packed Column									
Trays - Type									
Number									
Pleum Chamber									
Other									
Water Rate									
Design or Operating Temp. - °F									
Gas Rate - SCFM (lb./hr.)									
Moist (T-1), Ft.									
Diameter - Ft.									
Washed Cases to Stack									
Stack Height - Ft.									
Stack Diameter - Inches									
Installed Cost - \$/lb. S Labor - \$									
Operating Cost - \$/lb. S Labor - \$/lb. MAN/Yr.									
Operating Cost - Annual - \$									
Operating Cost - c/lb. MAN/Yr.									
Efficiency - %									

(a) Total cost of all pollution control devices plus incinerator is \$610,000.

WATER SCRIBERS

Flow Diagram Stream 1 D.

Device I. D. No.

EPA Code Number of plant

Purpose - Control Emission of

Type - Spray

Packed Column

Troves - Type

Number

Plenum Chamber

Other

Water Rate

Design or Operating Temp. - F°

Gas Rate - SCFM (lb./hr.)

Height (T-T), Ft.

Diameter - Ft.

Washed Cares to Stack

Stack Height - Ft.

Stack Diameter - Inches

Installed Cost - Mat'l. & Labor - \$

Operating Cost - Mat'l. & Labor - c/lb. MAN/Yr.

Operating Cost - Annual - \$

Operating Cost - c/lb. MAN/Yr.

Efficiency - %

TABLE MA-IV
CATALOG OF EMISSION CONTROL DEVICES
MALEIC ANHYDRIDE VIA
THE OXIDATION OF BENZENE

Page 2 of 3

MAN-5 18-4 Maleic Anhydride X	MAN-6 18-5 Maleic Anhydride Not Specified	MAN-7 18-6 Maleic Anhydride Not Specified	MAN-8 18-6 Maleic Anhydride Not Specified	MAN-9 18-7 Maleic Anhydride Not Specified	MAN-10 18-7 Maleic Anhydride X
Bubble Cap Not Specified					
17 - 37 GPM	Not Specified	Not Specified	Venturi	Not Specified	20 - 30 CPM
100	100	140	50	100	70 - 100
30,000	42,000	78,000	45	20,000	7,000
22.5	Not Specified	Not Specified	Not Specified	Not Specified	15
11	Not Specified	Not Specified	Not Specified	Not Specified	4
74	65	Not Specified	9.5		30
24	36	Not Specified	3		24
80,000	Not Specified	Not Specified	11,000	Not Specified	50,000
0.24			0.01		0.17
12,500			230		7,800
0.04			Unknown		0.03
Unknown					Unknown

INCINERATION DEVICES

Flow Diagram Stream 1, D.

Device I, D. No.
EPA Code Number of plant
Types of Compounds Incinerated
Type Device
Materials Incinerated, SCFM (lb./hr.)
Auxiliary Fuel Required (excl. pilot)
Auxiliary Fuel Type
Auxiliary Fuel Rate - $\frac{1}{2}$ BTU/hr.
Device Elevation - Ft. above grade
Installed Cost - Mat'l & Labor - \$
Installed Cost - Mat'l, & Labor - c/lb. of MAN
Operating Cost - Annual - \$
Operating Cost - c/lb. of MAN
Efficiency - CCR - %
Efficiency - SERR - %

TABLE MA-IV
CATALOG OF EMISSION CONTROL DEVICES
MALEIC ANHYDRIDE VIA
THE OXIDATION OF BENZENE

Page 3 of 3

MAN-11	Proposed
18-2	18-4
Aqueous Wastes	Organic Vapors, CO (b)
Incinerator	Boiler & Incinerator
(3400) Includes Water	30,000 Includes Air
Yes	Yes
Natural Gas	Natural Gas/oil
12 (Max.)	Not Specified
Not Specified (a)	Not Specified
	1,000,000 Total
	Not Applicable
	Not Available
	Not Available
99+ (Expected)	99+ (Expected)
Near 100 (c)	Near 100 (c)

(a) Total installed cost for all pollution control devices including scrubbers is \$610,000.

(b) Scrubber vent will supply combustion air to new gas/oil fired boiler-incinerator, which will eliminate odors, hydrocarbon emissions and carbon monoxide from this source. New boiler-incinerator will replace existing coal-fired boiler for steam generation.

(c) Depends upon time/temperature relationship for NO_x formation.

TABLE MA-V
NUMBER OF NEW PLANTS BY 1980

<u>Current Capacity</u>	<u>Marginal Capacity</u>	<u>Current Capacity on-stream in 1980</u>	<u>Demand 1980</u>	<u>Capacity 1980</u>	<u>Capacity to be Added</u>	<u>Economic Plant Size</u>	<u>Number of New Plants</u>
390	30	360	720	720	360	60	6

NOTE: All capacities in MM lbs./year.

TABLE MA-VI
EMISSION SOURCE SUMMARY*
TON/TON MALEIC ANHYDRIDE

Emission	Source	
	Scrubber Vent	Storage Losses and Fugitive Emissions
Hydrocarbons	.086	Note (1)
Particulates		Note (2)
NO _x		
SO _x		
CO	.670	

NOTES:

- (1) There will be small amounts of hydrocarbon emissions from storage tanks but the amount is not available.
- (2) Fugitive dust emissions will mostly be composed of maleic anhydride powder from the pelletizing, handling and storage operations of maleic anhydride. The amount is not indicated and will vary from plant to plant depending on operations.

TABLE MA-VII
WEIGHTED EMISSION RATES

Chemical	Maleic Anhydride			
Process	Oxidation of Benzene			
Increased Capacity by 1980		360 MM Lbs./Year		
Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	.086	31	80	2,480
Particulates			60	
NO _x			40	
SO _x			20	
CO	.670	241	1	241
Significant Emission Index =				2,721

Nylon 6

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	NYL-1
II. Process Description	NYL-2
III. Plant Emissions	NYL-3
IV. Emission Control	NYL-5
V. Significance of Pollution	NYL-6
VI. Nylon 6 Producers	NYL-7

List of Illustrations and Tables

Flow Diagram	Figure NYL-1
Net Material Balance	Table NYL-I
Gross Heat Balance	Table NYL-II
Emission Inventory	Table NYL-III
Catalog of Emission Control Devices	Table NYL-IV
Number of New Plants by 1980	Table NYL-V
Emission Source Summary	Table NYL-VI
Weighted Emission Rates	Table NYL-VII

I. Introduction

Nylon 6, $H[HN(CH_2)_5CO]_nOH$, is a linear aliphatic polyamide. It can be either spun into a fiber or made into a molding resin. The fiber is used for apparel, home furnishings, tire cord and industrial applications, while the resin is used for films, coatings for wires and cables, automotive parts and numerous other industrial and consumer applications.

Nylon 6 is produced commercially by the continuous polymerization of caprolactam, $HN(CH_2)_5CO$.

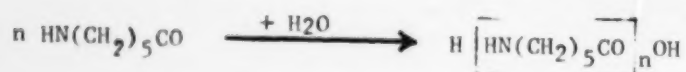
In the old process the polymer was produced by batch polymerization, but because the reaction produces no water it was relatively easy to put the process on a continuous basis. Small quantities of the polymer are still produced by the old method.

Today, nylon 6 capacity stands at around 500 MM lbs./year. It is expected that by 1980 the capacity will reach 1.5 billion lbs./year, requiring about ten new nylon 6 plants each having a capacity of 100 MM lbs./year.

Air emissions associated with nylon 6 polymerization are caused by small vents from numerous process operations. In general, the process could be characterized as a moderately low polluter.

II. Process Description

Nylon 6 is produced by the continuous polymerization of caprolactam.



The mechanism of the reaction is considered to involve an addition reaction of an open lactam ring into the growth chain initiated by the combined catalytic effect of water and acid groups. Contrary to amino acid polymerization, the reaction does not involve any significant removal of water since only small amounts are used as catalyst. The overall reaction is an equilibrium reaction with conversions of monomer of 85 to 90%. A substantial amount of oligomers (5%) are formed and they must be removed in part (1-2% of product) if high quality polymer is desired.

The following is a description of a typical process to produce nylon 6 (see Figure NYL 1).

Molten caprolactam is mixed with water, catalysts, stabilizer and delusterant (if fibers are to be made) and is fed into a reactor which is operated at about 500° F. The mass slowly proceeds down the reactor which is usually divided into several zones. The overall reaction is slightly exothermic and heat exchange is provided by dowtherm. The reactor effluent consists of molten polymer, monomer, oligomers and water. Monomer and oligomer constitute 10-15% of the reactor effluent.

There are two methods being used to purify the crude polymer and recover unreacted polymer. In the first, the polymer is cast into ribbon form, quenched and cut into chips. Unreacted monomer and some oligomer are removed from the chips by extraction with hot water. The water is sent to monomer recovery where the oligomers are depolymerized and the monomer is dehydrated and returned to the system. The chips are dried and are then ready for melting and spinning or bagging.

In the second method, the molten polymer exiting from the reactor is sent to a vacuum distillation column where monomer, water and oligomers are removed overhead. The molten polymer can then be spun directly into fibers or cut into chips for bagging.

III. Plant Emissions

A. Continuous Air Emissions

A majority of the air pollution associated with nylon 6 polymerization is caused by small vents from a number of process units. Although plant 19-3 was the only respondent to report any emission control devices from these sources, it is believed that other producers use vent condensers to recover some caprolactam. The following is a description of the sources of air emissions from the nylon 6 process.

1. Mix and Spin Tank Vents

Only respondent 19-4 reports losses due to the mixing of molten caprolactam with water and catalysts prior to reaction. Since the system is nitrogen padded, the main constituent of this vent is nitrogen. The only noxious emission is .00012 lbs./lb. nylon 6 of caprolactam.

2. Polymerization Vent

Nitrogen present as an inert in the reaction chamber along with some water is purged from the system by venting from the polymerization reactor. Some caprolactam is carried with the gases to the atmosphere. Emission rates vary from plant to plant but on the average, about .00034 lbs./lb. nylon 6 of caprolactam enters the atmosphere from this source.

3. Chip Formation Vent

When the molten polymer ribbon is quenched with either cold water or an inert gas, some caprolactam vapor is lost to the atmosphere before the polymer solidifies. Plant 19-3 reports significant emissions of .00337 lbs./lb. of nylon 6 of caprolactam.

4. Nylon Chip Slurry Tank

Plant 19-4 reports small losses of caprolactam from the slurry tank prior to the extraction system.

7. Depolymerizer Vent

Oligomers extracted from the product are in many plants depolymerized to caprolactam. Some caprolactam is usually vented to the atmosphere from the depolymerizing reactor. The quantity released varies from insignificant to significant quantities.

6. Pellet Drying

Small amounts of caprolactam are lost when the extracted pellets are dried with an inert gas or air. The quantity released to the atmosphere is small.

8. Caprolactam Recovery Vent

Plant 19-3 reports that trace amounts of caprolactam are lost during the caprolactam recovery distillation process.

B. Intermittent Air Emissions

1. Equipment Cleaning Furnaces

Equipment such as filters, etc., which become fouled with polymer and oligomers are cleaned, in some operations, in a furnace. The two respondents which report such operations claim that only carbon dioxide and water are emitted. One of the plants reports an afterburner, without which, smoking will probably occur.

C. Continuous Liquid Waste

1. Waste Water

Waste water discharges and methods of treatment used by nylon 6 producers are summarized below.

<u>Plant Code No.</u>	<u>Waste Water - GPM</u>	<u>Treatment Used</u>
19-1	.12	Not Specified
19-3	20-50 (cooling water)	Chlorine Treated Evaporative Ponds (Reclaimed)
19-4	.5 (process) 1.8 (cooling)	Untreated Untreated

D. Solid Wastes

Solid waste in the form of oligomers and waste polymer is produced at many installations. The waste can be disposed of in a land fill.

E. Odor

There are no community odor problems associated with the nylon 6 polymerization process.

F. Fugitive Emissions

No sources of air emissions due to leaks, spills, etc., were reported. It is assumed that such losses exist but are not significant.

G. Noise

Although not reported, or requested in the questionnaire, it has been reported by industry that noise from cutters may be an environmental problem.

IV. Emission Control

Details on emission control devices reported by the respondent can be found in Table IV, Catalog of Emission Control Devices. A brief description of the devices follows:

Condensers

Plant 19-3 employs vent condensers to lower emissions and increase recovery of caprolactam from the polymerization reactor vent and the caprolactam recovery column vent.

Scrubbers

Spray type scrubbers are employed in plant 19-3 to reduce emissions from the pelletizer vent and the depolymerizer vent.

Afterburner

Plant 19-3 employs an afterburner to insure that only carbon dioxide and water exit from the equipment cleaning furnace. The operator reports that the exhaust is smokeless and odorless so complete combustion is assumed.

V. Significance of Pollution

It is recommended that no in-depth study be made of the subject process. The quantity of air emissions released as air pollutants is less for this process than for processes currently under in-depth study.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index of 194 has been calculated in Table VII. Hence, the recommendation to exclude an in-depth study of Nylon 6 Polymerization from the overall scope of work for this project.

NYL-7

VI. Nylon 6 Producers

<u>Company</u>	<u>Location</u>	<u>Capacity - MM Lbs./Year</u>
Allied Chemical Co.	Chesterfield, Va.	238
American Enka Corp.	Enka, N. C.	79
	Lowland, Tenn.	20*
Dow Badische Co.	Freeport, Texas	80
Firestone Tire & Rubber Co.	Hopewell, Va.	47
	Pottstown, Pa.	2*
Foster Grant Co.	Leominster, Mass.	5*
Gulf Oil Corp.	Henderson, Ky.	5*
Rohm & Haas Co.	Fayetteville, N. C.	<u>10*</u>
		Total - 486

*Capacities are approximate.

TABLE NYL-I
MATERIAL BALANCE
NYLON 6 (1)
T/T NYLON 6

<u>Fresh</u> <u>Caprolactam</u>	<u>Recycle</u> <u>Caprolactam (2)</u>	<u>Polymer</u>		<u>Waste</u> <u>(Oligomers &</u> <u>Waste Polymer)</u>
		<u>Nylon 6</u>	<u>Oligomers</u>	
1.147	.146	.985	.015	.001

(1) Based on information found in literature and respondents comments.

(2) Unreacted caprolactam and caprolactam recovered from oligomer depolymerization.

TABLE NYL-II
HEAT BALANCE
NYLON 6

There is insufficient information available on which to base an overall energy balance for Nylon 6 polymerization.

Plant EPA Code Number	Stream I.D. No. (Figure NYL-1)	Hot Melt Filter Vent	Vacuum Jet Exhaust	Pellet Drying	Vaporized Benzene from Waste Water	Equipment Cleaning Furnace Afterburner Exhaust
Capacity - Tons/Yr. of Nylon 6 Production - Tons/Yr. of Nylon 6 Emissions to Atmosphere	19-1 40,000 40,000					
Flow - lbs./hr. Flow Characteristic - Continuous or Intermittent if Intermittent - hr./yr.	D Pellet Drying					Equipment Cleaning Furnace Afterburner Exhaust
Composition - Ton/Ton of Nylon 6 Caprolactam	Never Measured Continuous	6200 SCFM Continuous		1363 Continuous	Continuous	~318 SCFM Intermittent alb
Benzene	+ (2)	.000001			.003852	
Nitrogen	(1) (1)			.143169 .005618		(3) (3)
Water	Yes			.000153		
Carbon Dioxide	1					
Oligomer	36					
Phosphoric Acid	19.5 by 14.5					
Hydrogen	100					
Vent Stacks	6200					
Number	No					
Height - Feet	Yes					
Diameter - Inches	1					
Exit Gas Temp. - F°	46					
Flow - SCFM	90					
Emission Control Devices	No					
Type	No					
Analysis	Yes					
Sample Tap Location	None					
Date or Frequency of Sampling	March, 1972					
Type of Analysis	Chromatograph					
Odor Problem	No					
Summary of Air Pollutants						
Hydrocarbons - Ton/Ton of Nylon 6						
*Particulates & Aerosols - Ton/Ton of Nylon 6						
NOx - Ton/Ton of Nylon 6						
SOx - Ton/Ton of Nylon 6						
CO - Ton/Ton of Nylon 6						

*Caprolactam vapors are considered a severe skin irritant.

(1) Mostly water and air.

(2) Mostly air.

(3) Complete combustion to CO_2 and H_2O reported.

TABLE NYL-III
NATIONAL EMISSIONS INVENTORY
NYLON 6

Page 2 of 3

Plant EPA Code Number	19-2	Confidential (1)	
Capacity - Tons/Yr. of Nylon 6	Confidential	Confidential	
Production - Tons/Yr. of Nylon 6			
Emissions to Atmosphere			
Stream I. D. No. (Figure NYL-1)	B	Depolymerizer Vent	
Stream	Chip Polymerizer		
	22	477	
	Continuous	Continuous	
	+	+	
	Nearly 100	Nearly 100	
Flow - lbs./hr.			
Flow Characteristic - Continuous or Intermittent			
If Intermittent - Hrs./Yr.			
Composition - Ton/Ton of Nylon 6			
Caprolactam			
Benzene			
Nitrogen			
Air			
Water			
Carbon Dioxide			
Oilsomer			
Phosphoric Acid			
Hydrogen			
Vent Stacks			
Number	Yes	Yes	
Height - Feet	1	1	
Diameter - Inches	70	70	
Exit Gas Temp. - F°	144	144	
Flow - SCFH	250	250	
Emission Control Devices			
Type	Yes	Yes	
	Vent Condenser	Vent Condenser	
	None	None	
Analysis			
Sample Tap Location			
Date or Frequency of Sampling			
Type of Analysis			
Odor Problem			
Summary of Air Pollutants			
Hydrocarbons - Ton/Ton of Nylon 6	0		
Particulates & Aerosols - Ton/Ton of Nylon 6	+		
NO _x - Ton/Ton of Nylon 6	0		
SO _x - Ton/Ton of Nylon 6	0		
CO - Ton/Ton of Nylon 6	0		
Material Balance			
No	Material Balance	Material Balance	
	No	No	

(1) Published capacity is 45 up lbs./year.

52

TABLE NYL-III
NATIONAL EMISSIONS INVENTORY
NYLON 6

Page 4 of 5

Plant EPA Code Number:	19-4				
Capacity - Tons/Yr. of Nylon 6	39,275				
Production - Tons/Yr. of Nylon 6	39,275				
Emissions to Atmosphere					
Stream I. D. No. (Figure NYL-1)					
Stream					
	A	B	C	D	
	Mix Tank Vents	Spin Tank Vents	Polymerization Reactor Vent	Part Cleaning Furnace Off-Gas	Depolymerization Reactor Vent
Flow - Lbs./Hr.	Continuous	Continuous	Continuous	Intermittent	Continuous
Flow Characteristic - Continuous or Intermittent				Not Specified	
if Intermittent - Hrs./Yr.					
Composition - Ton/Ton of Nylon 6					
Caprolactam	.000005	.000118	.000100		(2)
Benzene	.000195	.001433	.003233		254220
Nitrogen			.000016	(1)	
Air				(1)	
Water	.000001				(2)
Carbon Dioxide					(2)
Oligomer					
Phosphoric Acid					
Hydrogen					
Vent Stacks	Not Specified	Not Specified	Not Specified	Not Specified	Not Specified
Number					
Height - Feet					
Diameter - Inches					
Exit Gas Temp. - F					
Flow - SCFM					
Emission Control Devices	No	No	No	No	No
Type	None	None	None	None	None
Analysis	Estimate	Estimate	Estimate	None	None
Sample Tap Location					
Date or Frequency of Sampling					
Type of Analysis					
Odor Problem					
Summary of Air Pollutants					
Hydrocarbons - Ton/Ton of Nylon 6			0		
*Particulates & Aerosols - Ton/Ton of Nylon 6			.0263		
NO _x - Ton/Ton of Nylon 6			0		
SO _x - Ton/Ton of Nylon 6			0		
CO - Ton/Ton of Nylon 6			0		

(1) Composition unknown.

(2) A total of 3 vol. %, approximately 026 lbs /lb. nylon 6 (not considered typical).

INCINERATION DEVICES

EPA Code No. for plant using

Device I. D. No.

Type of Compound Incinerated

Type of Device

Material Incinerated - SCFM

Auxiliary Fuel - Excluding Pilot

Type

Rate - BTU/hr.

Device or Stack Height - Feet

Installed Cost - Mat'l. & Labor - \$

Installed Cost Based on "year" - dollars

Installed Cost - c/lb. of Nylon 6/year

Operating Cost - Annual - \$ (1972)

Net Value of Recovered Heat

Net Operating Cost - \$/year

Net Operating Cost - c/lb. of Nylon 6

Efficiency - CCR (1)

TABLE NYL-IV
CATALOG OF EMISSION CONTROL DEVICES
NYLON 6

19-1	
IN-1	Hydrocarbon and CO (1)
After Burner	
800	
Yes	
Methane	
9.6	
7,700	
1971	
.0096	
1900	
1900	
.0024	
100%	

Page 1 of 2

(1) For explanation and definition see Appendix V.

SCRUBBERS

EPA Code No. for plant using
Flow Diagram (Fig. Nylon 1) Stream No.

Device I. D. No.

Control Emission of

Scrubber Type

Scrubbing Liquid

Scrubbing Liquid Rate - GPM

Operating Temp. - F°

Gas Rate - SCFM

Washed Gases to Stack

Stack Height - Ft.

Stack Diameter - Inches

Installed Cost - Mat'l. & Labor - \$

Installed Cost based on "year" - dollars

Installed Cost - c/lb. of Nylon 6/year

Operating Cost - Annual - \$

Value of Recovered Product - \$

Net Operating Cost - c/lb. of Nylon 6

Efficiency - % - SE (1)

Efficiency - % - SERR (1)

TABLE NYL-10
CATALOG OF EMISSION CONTROL DEVICES
NYLON 6

Page 2 of 2

19-3
F
SC-11
Caprolactam
Duct Spray
Water

Yes
65
12 by 12
40,200
1961
.017

19-3
C
SC-1
Caprolactam
Spray Eductor
Water

Yes
95
12
45,000
1973
.018
2200
.009

Stream Ejector and Condenser

19-3
F
COS-11
Caprolactam
Steam

Trace
1,500
1968
.006
1400
1400
(.006)
Near 100
Near 100%

Heat Exchanger

19-3
B
COS-1
Caprolactam
Water

~700

60,000
1961 - 1970
.025
11,000
340,000
329,000
(.138)

CONDENSERS

EPA Code No. for plant using
Flow Diagram (Fig. Nylon 1) Stream No.

Device I. D. No.

Control Emission of

Cooling Liquid

Cooling Liquid Rate

Gas Rate - SCFM

Temperature to Condenser - F°

Temperature out of Condenser - F°

Quantity Condensed - lbs./hr.

Non-Condensibles - SCFM

Installed Cost - Mat'l. & Labor - \$

Installed Cost based on "year" - dollars

Installed Cost - c/lb. of Nylon 6/year

Operating Cost - Annual - \$ (1972)

Value of Recovered Product - \$

Net Operating Cost - Annual - \$

Net Operating Cost - c/lb. of Nylon 6

Efficiency - % - SE (1)

Efficiency - % - SERR (1)

TABLE NYL-V
NUMBER OF NEW PLANTS BY 1980
NYLON 6

Current Capacity (1)	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity to be Added	Economic Plant Size	Number of New Units
486	0	486	1500 (2)	1014	100	10

(1) MM lbs./year.

(2) Process Research, Inc., report for the EPA.

TABLE NYL-VI
EMISSION SOURCE SUMMARY
NYLON 6
T/T NYLON 6

Pollutant	Source					Total
	Mixing Tank Vents	Reactor Vent	Pellet Formation Washing & Drying Vents	Furnace Cleaning	Caprolactam Recovery	
Hydrocarbon	0	0	0	0	0	0
Aerosols & Particulates (1)	.00012	.00034	.00172	0	0.001	0.00318
NO _x	0	0	0	Trace	0	Trace
SO _x	0	0	0	0	0	0
CO	0	0	0	0	0	0

(1) Caprolactam is considered an aerosol.

TABLE NYL-VII
WEIGHTED EMISSION RATES

Chemical Nylon 6
Process Continuous Polymerization of Caprolactam
New Added Capacity 1,014 MM Lbs./Year

Pollutant	Emissions, lb./Lb.	Increased Emissions MM lbs./Year	Weighting Factor	Weighted Emissions MM lbs./Year
Hydrocarbons	0	0	80	0
Aerosols & Particulates (1)	.00318	3.2	60	194
NO _x	Trace	0	40	0
SO _x	0	0	20	0
CO	0	0	1	0
Significant Emission Index = 194				0

Nylon 6,6

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	N6,6-1
II. Process Description	N6,6-2
III. Plant Emissions	N6,6-4
IV. Emission Control	N6,6-6
V. Significance of Pollution	N6,6-7
VI. Nylon 6,6 Producers	N6,6-8

List of Illustrations and Tables

Flow Diagram	Figure N-I
Net Material Balance	Table N6,6-I
Gross Heat Balance	Table N6,6-II
Emission Inventory	Table N6,6-III
Catalog of Emission Control Devices	Table N6,6-IV
Number of New Plants by 1980	Table N6,6-V
Emission Source Summary	Table N6,6-VI
Weighted Emission Rates	Table N6,6-VII

I. Introduction

Nylon 6,6 is synthesized from its monomer, hexamethyl diammonium adipate or nylon salt, by polymerizing the monomer to a molecular weight of 12,000 to 20,000 under temperature and pressure. Nylon salt is made by neutralization of aqueous solutions of its components, hexamethylene diamine and adipic acid.

There are two processes used to make nylon 6,6. The older process is batch polymerization, which usually ends with the nylon 6,6 as a flake or pellet, which may then be remelted and spun to yarn. The second process, the newer of the two, is a continuous polymerization and spinning process, which produces a nylon yarn or filament directly.

Although there is a large installed capacity for nylon 6,6 production, some 1.5 billion pounds annually, the amount of air pollution associated with these plants is comparatively small on a mass emission basis. However, depending on plant size, the emissions which can produce a "blue haze" may become sufficiently significant to make their abatement desirable. In such circumstances the most conventional abatement approach is scrubbing. This produces a biodegradable liquid waste. One plant estimates a \$4 million investment in its combined air-liquid abatement facilities. A modest amount of solid waste is generated which has no commercial value.

II. Process Description

Nylon 6,6 is made by polymerization of nylon salt (hexamethylene diammonium adipate) from an aqueous suspension at elevated temperature and pressure. Two processes are in general use, batch and continuous. Nylon salt is usually stored as a 10 - 20% aqueous solution and can easily be made from aqueous solutions of adipic acid and hexamethylene diamine.

Batch Process - the reaction is:

(a) Neutralization



Adipic Acid

Hexamethylene
Diamine

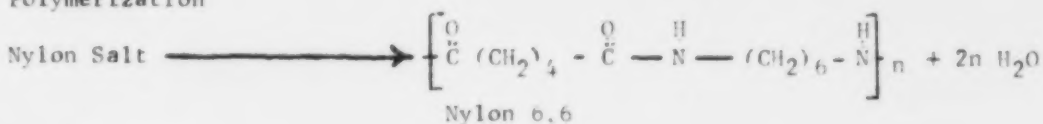
Hexamethylene Diammonium Adipate
(Nylon Salt)

Mol. Wt. 146.1

116.2

262.3

(b) Polymerization



Mol. Wt. (repeat unit) 226.8

Nylon monomer (nylon salt) is usually fed as a water suspension or homogeneous mixture to an evaporator where it is concentrated to a 50 - 60% aqueous slurry by removal of water. This aqueous slurry together with additives such as 0.5% by weight acetic acid as a chain terminator (viscosity, m. wt. control), TiO_2 as a delusterant, are pumped to an autoclave reactor. Here temperature is increased to $260^\circ - 280^\circ \text{C}$ ($\approx 520^\circ \text{F}$) and pressure is allowed to build to 250 PSIG by controlled venting of the steam produced from the condensation polymerization. Any water remaining after this point is reached is then removed by lowering the pressure to atmospheric while maintaining a constant temperature. The polymer (12,000 - 20,000 m.v.) is a clear melt which is removed from the reactor under nitrogen, cooled and cast (pelletized) quickly as it is not stable at high temperatures. The solid nylon 6,6 resin is flaked or chipped and can then go to product storage. These flakes can be remelted and spun into filaments or molded to various shapes.

Continuous Process

A more recent development in nylon 6,6 manufacture is the continuous process. The chemistry of this reaction is identical to the batch process. However, where it may take 2 - 4 hours to convert nylon salt to finished polymer in the batch process, monomer goes to polymer in the continuous process in about 5 minutes, but with a relatively higher investment per unit produced.

Nylon salt solution is fed to a thin film evaporator at about 230°F , where the bulk of the water of solution is removed. Any additives needed are generally added after the evaporation stage and these plus the dewatered monomer are fed to another thin film evaporator held at 450°F and elevated pressure where the condensation polymerization takes place and the water is removed as steam. Molten polymer goes to a "flasher" at atmospheric pressure to remove more water of condensation. The polymer may be put thru a finishing

Nylon 6,6-3

step at 540° F to be sure polymerization is complete or it may by-pass this step. In any event the hot molten polymer goes directly to spinning, drawing and beaming operations rather than cooling and casting into resin as in the batch process.

III. Plant Emissions

A. Continuous Air Emissions - Batch & Continuous Processes

1. Evaporator Off-Gas - Code Letter (A) on drawing

Both respondents report essentially all steam from this source with very small traces of hexamethylene diamine present. No scrubbing or incinerator devices are used. No odors were reported.

2. Reactor or Polymerizer Off-Gas - Code Letter (B) on drawing

Again the main constituent of this vent stream is steam with small amounts of hexamethylene diamine. The presence of monomer and polymer is noted as detectable and has the potential for causing off-plant odors. One plant is installing scrubbers to control this potential odor source and the attendant "blue haze" which periodically forms.

3. Flasher or Separator Off-Gas - Continuous Process - Vent (C)

This stream is reported to be similar in composition to the reactor off-gas (code letter C) but much less in terms of lb. gas per lb. finished product. No odors were reported.

4. Finisher Exhaust - Code Letter (D) - Continuous Process

Not all continuous processes employ a finishing step after the high pressure reaction - atmospheric pressure flashing step. Those that do, report very small emissions compared to the other stages. This stream is normally not scrubbed although one respondent scrubs this stream with a water spray in some of his units. No odor problems were reported.

5. Miscellaneous Streams

(a) When the flaked nylon resin is pneumatically conveyed, the conveying gas can be a source of emissions to the atmosphere. The one piece of data on this stream, a cyclone exhaust shows only minimal traces of water vapor, hexamethylene diamine and nylon.

(b) One respondent showed an emission from the spinning operation. Presumably this is cooling air contaminated with infinitesimal quantities of particulates, hydrocarbons and nylon 6,6. The stream was not scrubbed and no estimate of quantity was available.

(c) Nylon scraps (see also D-Solid Wastes). One respondent reports incineration of about 0.003 lb. nylon scraps per lb. nylon 6,6. Complete incineration of the scraps would give roughly 0.00123 lb. NO_x per lb. nylon 6,6. No data on this incineration are available.

B. Intermittent Air Emissions

No intermittent air emissions were reported.

Nylon 6,6-5

C. Continuous Liquid Wastes

Only one respondent reported waste water quantities from the processes as follows:

<u>Process Type</u>	<u>Waste Water from</u>	<u>GPM</u>	<u>Treatment</u>
Batch	Casting	36	in-plant
Continuous	Not Specified	135	in-plant

D. Solid Wastes

Operator of plant EPA code 20-1 reports production of 1,160 lbs. per day of casting scraps (nylon polymer), which are incinerated. Plant code EPA 20-3, a continuous process reports "no solid wastes associated with this process". No comment was available from another respondent.

E. Odors

The polymerization of nylon salt to nylon 6,6 is a process for which no odor problems or complaints were reported. The odor of hexamethylene diamine is detectable at times on site and under some atmospheric conditions it may also be detected beyond the plant borders.

F. Fugitive Emissions

Neither respondent reports any fugitive losses. The only comment was that there are "no other known emissions although minor leakages probably occur".

G. Other Emissions

Fuel oil for heating was reported by only one respondent. About 56 million lbs. of fuel oil are consumed at a maximum of 3% sulfur (estimated average is 2.5%). At the maximum level, this is 1.7 million lbs. of S per year or 3.4 million lbs. SO₂ per year, the largest single reported source of pollution in the process (0.0093 lbs. SO₂/lb. nylon 6,6).

Dowtherm is used for a heat transfer medium. Losses here are 75 gal./year (one source of data), which is insignificant.

IV. Emission Control

Two plants report using emission control devices. One instance is a water scrubber used on the exhaust from the finishing operations. Water is the scrubbing medium and the effluent is treated in-plant before discharge to the sewer. The following efficiencies were calculated on the basis of reported data.

SE* - Specific Efficiency - 99.7%.

SERR* - Significance of Emission Reduction Rating - 99.7%.

The other plant is in the process of adding scrubbers to their polymerizer equipment which they consider to be the major source of air pollution from the process ("blue haze" and hexamethylene diamine odor).

*See Appendix V for explanation of these terms.

V. Significance of Pollution

It is recommended that no in-depth study of this process be made. Emissions are low and roughly equal to the combustion product emissions from the fuels used in some of the plants.

A modest 10% per year growth is projected for the period up to 1980. Even if this growth were off by 50 to 100%, the Significance of Emission Index* would still be low. An SEI of 318 has been calculated for this process. Doubling this figure would still leave the process in the low pollution category. Emissions consist mostly of particulates (hexamethylene diamine is the major component), which could easily be removed by water scrubbing (as one respondent is doing) should this ever be necessary.

*See Appendix IV for an explanation of this term.

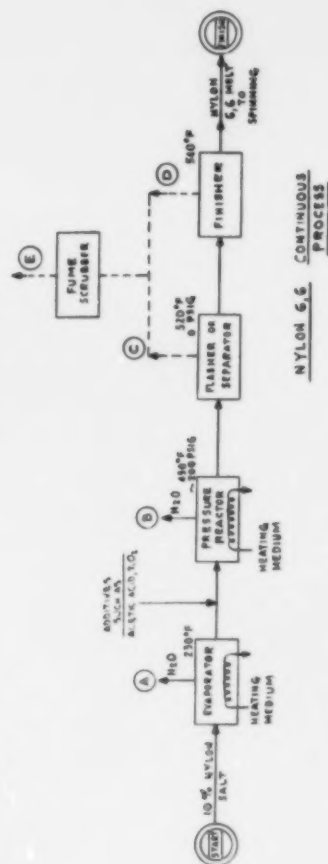
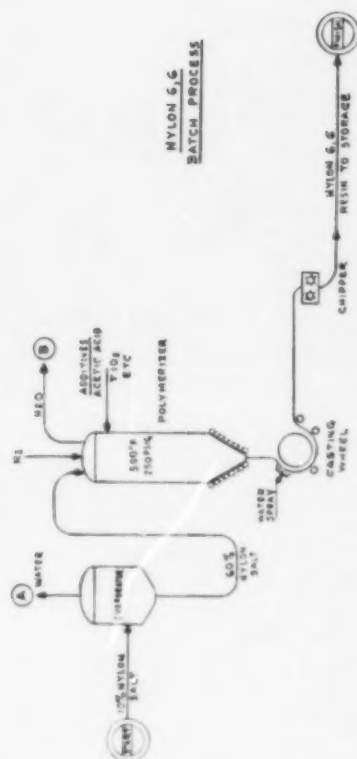
Nylon 6,6-8

VI. Producers of Nylon 6,6 Resins and Fibres from Monomer

The capacities and plant locations listed below are based on information provided in the questionnaire and in the literature.

<u>Company</u>	<u>Location</u>	MM Lbs. <u>1971 Capacity</u>
<u>Fibre Producers</u>		
Allied Chem. Fibres Div.	W. Conshohocken, Pa.	N. A.
E. I. duPont	Camden, S. C.	40
	Chattanooga, Tenn.	140
	Martinsville Va.	100
	Richmond, Va.	200
	Seaford, Del.	365
Beaunit Corporation	Etowah, Tenn.	
	Odessa, Texas	100
Fibre Industries, Inc.	Greenville S. C.	80
	Cuazama, P. R.	60
Monsanto	Greenwood, S. C.	100
	Pensacola, Florida	240
Rohm & Haas, Sauquoit Fibres Div.	Scranton, Pa.	4
		Sub - 1,429

<u>Resin Producers</u>		
Celanese Corporation	La Porte, Texas	12
DuPont Plastics Department	Parkersburg, W. Va.	70
Beaunit Corporation	Etowah, Tenn.	2
Monsanto Corporation	Pensacola, Florida	10
		Total - 1,523



NOTE: REFER TO TABLE III
FOR LISTING OF TYPES
OF EMISSION SYSTMS;
FOR EXAMPLE, (A) CARBON DIOXIDE

[illegible]

TABLE N6,6-1
MATERIAL BALANCE

The conversion of nylon 6,6 salt (hexamethylene diammonium adipate) to nylon 6,6 polymer is almost 100% of theoretical according to the literature and data surveyed. A comparison of actual reported yields vs theoretical is shown below:

<u>Source</u>	<u>Lb. Adipic Acid per Lb. Nylon 6,6</u>	<u>Lb. Hexamethylene Diamine per Lb. Nylon 6,6</u>	<u>Lb. Nylon 6,6 Polymer</u>	<u>Lb. Water per Lb. Nylon 6,6</u>
Theory	0.646	0.513	1.000	0.159
Actual	0.653	0.521	1.000	0.174*

*includes waste products which are reported minimal.

TABLE N6,6-II
CROSS REACTOR HEAT BALANCE

There are not sufficient published data available to permit the construction of a detailed heat balance for this proces.

TABLE No. 6-III
NATIONAL EMISSION INVENTORY
Emissions from Nylon Salt

Plant Code No. Capacity - Tons Nylon 6,6/year Range in Production - % of Max. Emissions to Atmosphere Stream	Flow - lbs./hr. Flow Characteristic Composition, Ton/Ton Nylon 6,6	20-1			20-2		
		None	75,000 None	None	None	93,500	None
		(A) - Vaporator Off-gas	(B) Autoclave Off-gas	(C) Conveyor Air Exhaust	(A) - Vaporator Off-gas	(B) - Autoclave Off-gas	
		4700 Continuous	540 Continuous	7500 Continuous	4708 Continuous	610 Continuous	
		+	+	+	+	+	
		0.274700	0.031480		1.10500	0.61000	
		0.000175	0.000090		0.00090	0.00200	
		+	+	+			
		1	1	1	5	21	
		10	26	Cyclone	86	86	
		8	4		8	4	
		1550	4000	1290	3.00	3000	
		1665	178	5400	1.50	216	
		None	None	None	None	None	
		Never	Never	Never	Occasional	Occasional	
		Calc'd.	Calc'd.	Calc'd.	TIT, (C, GRAV, TOC No	TIT, GC, GRAV, TOC No	
		0	0	0		0	
		0.000265	0.000265	0.002900		0.002900	
		0	0	0		0	
		0	0	0		0	
		0	0	0		0	

Summary of Air Pollutants
Hydrocarbons, Ton/Ton Nylon 6,6
Particulates & Aerosols - Ton/Ton Nylon 6,6
SOx - Ton/Ton Nylon 6,6
NOx - Ton/Ton Nylon 6,6

plant Code No.

Capacity - Tons Nylon 6,6/Year

Place in Production - of Max

Emissions to Atmosphere

Stream

Flow - lbs /hr

Flow Characteristic

Composition, ton/Ton Nylon 6,6

Nylon Salt

Water

Hexamethylene Diamine

Adipic Acid

Nylon 6,6 Polymer

Cyclopentanone

Halides

Tot Organic Carbon

Sulfonamide

Cent Stacks

Number

Height - Feet

Diameter - Inches

Exit Gas Temp., of

SCM/Stack

Emission Control Devices

Type

Analyses

Date or Frequency of Sampling

Sample Location

Type of Analysis

Odor Problem

Summary of Air Pollutants

Hydrocarbons - Ton/Ton Nylon 6,6

Particulates & Aerosols - Ton/Ton Nylon 6,6

M_g - Ton/Ton Nylon 6,6

SO_x - Ton/Ton Nylon 6,6

Cl₂ - Ton/Ton Nylon 6,6

1990

73

TABLE No. 6-III
NATIONAL EMISSIONS INVENTORY
NYLON 6,6 FROM NYLON 6,6

Plant Code No.	20-2	20-3	20-4	20-5	20-6	20-7	20-8	20-9	20-10	20-11	20-12	20-13	20-14	20-15	20-16	20-17	20-18	20-19	20-20	20-21	20-22	20-23	20-24	20-25	20-26	20-27	20-28	20-29	20-30	20-31	20-32	20-33	20-34	20-35	20-36	20-37	20-38	20-39	20-40	20-41	20-42	20-43	20-44	20-45	20-46	20-47	20-48	20-49	20-50	20-51	20-52	20-53	20-54	20-55	20-56	20-57	20-58	20-59	20-60	20-61	20-62	20-63	20-64	20-65	20-66	20-67	20-68	20-69	20-70	20-71	20-72	20-73	20-74	20-75	20-76	20-77	20-78	20-79	20-80	20-81	20-82	20-83	20-84	20-85	20-86	20-87	20-88	20-89	20-90	20-91	20-92	20-93	20-94	20-95	20-96	20-97	20-98	20-99	20-100	20-101	20-102	20-103	20-104	20-105	20-106	20-107	20-108	20-109	20-110	20-111	20-112	20-113	20-114	20-115	20-116	20-117	20-118	20-119	20-120	20-121	20-122	20-123	20-124	20-125	20-126	20-127	20-128	20-129	20-130	20-131	20-132	20-133	20-134	20-135	20-136	20-137	20-138	20-139	20-140	20-141	20-142	20-143	20-144	20-145	20-146	20-147	20-148	20-149	20-150	20-151	20-152	20-153	20-154	20-155	20-156	20-157	20-158	20-159	20-160	20-161	20-162	20-163	20-164	20-165	20-166	20-167	20-168	20-169	20-170	20-171	20-172	20-173	20-174	20-175	20-176	20-177	20-178	20-179	20-180	20-181	20-182	20-183	20-184	20-185	20-186	20-187	20-188	20-189	20-190	20-191	20-192	20-193	20-194	20-195	20-196	20-197	20-198	20-199	20-200	20-201	20-202	20-203	20-204	20-205	20-206	20-207	20-208	20-209	20-210	20-211	20-212	20-213	20-214	20-215	20-216	20-217	20-218	20-219	20-220	20-221	20-222	20-223	20-224	20-225	20-226	20-227	20-228	20-229	20-230	20-231	20-232	20-233	20-234	20-235	20-236	20-237	20-238	20-239	20-240	20-241	20-242	20-243	20-244	20-245	20-246	20-247	20-248	20-249	20-250	20-251	20-252	20-253	20-254	20-255	20-256	20-257	20-258	20-259	20-260	20-261	20-262	20-263	20-264	20-265	20-266	20-267	20-268	20-269	20-270	20-271	20-272	20-273	20-274	20-275	20-276	20-277	20-278	20-279	20-280	20-281	20-282	20-283	20-284	20-285	20-286	20-287	20-288	20-289	20-290	20-291	20-292	20-293	20-294	20-295	20-296	20-297	20-298	20-299	20-300	20-301	20-302	20-303	20-304	20-305	20-306	20-307	20-308	20-309	20-310	20-311	20-312	20-313	20-314	20-315	20-316	20-317	20-318	20-319	20-320	20-321	20-322	20-323	20-324	20-325	20-326	20-327	20-328	20-329	20-330	20-331	20-332	20-333	20-334	20-335	20-336	20-337	20-338	20-339	20-340	20-341	20-342	20-343	20-344	20-345	20-346	20-347	20-348	20-349	20-350	20-351	20-352	20-353	20-354	20-355	20-356	20-357	20-358	20-359	20-360	20-361	20-362	20-363	20-364	20-365	20-366	20-367	20-368	20-369	20-370	20-371	20-372	20-373	20-374	20-375	20-376	20-377	20-378	20-379	20-380	20-381	20-382	20-383	20-384	20-385	20-386	20-387	20-388	20-389	20-390	20-391	20-392	20-393	20-394	20-395	20-396	20-397	20-398	20-399	20-400	20-401	20-402	20-403	20-404	20-405	20-406	20-407	20-408	20-409	20-410	20-411	20-412	20-413	20-414	20-415	20-416	20-417	20-418	20-419	20-420	20-421	20-422	20-423	20-424	20-425	20-426	20-427	20-428	20-429	20-430	20-431	20-432	20-433	20-434	20-435	20-436	20-437	20-438	20-439	20-440	20-441	20-442	20-443	20-444	20-445	20-446	20-447	20-448	20-449	20-450	20-451	20-452	20-453	20-454	20-455	20-456	20-457	20-458	20-459	20-460	20-461	20-462	20-463	20-464	20-465	20-466	20-467	20-468	20-469	20-470	20-471	20-472	20-473	20-474	20-475	20-476	20-477	20-478	20-479	20-480	20-481	20-482	20-483	20-484	20-485	20-486	20-487	20-488	20-489	20-490	20-491	20-492	20-493	20-494	20-495	20-496	20-497	20-498	20-499	20-500	20-501	20-502	20-503	20-504	20-505	20-506	20-507	20-508	20-509	20-510	20-511	20-512	20-513	20-514	20-515	20-516	20-517	20-518	20-519	20-520	20-521	20-522	20-523	20-524	20-525	20-526	20-527	20-528	20-529	20-530	20-531	20-532	20-533	20-534	20-535	20-536	20-537	20-538	20-539	20-540	20-541	20-542	20-543	20-544	20-545	20-546	20-547	20-548	20-549	20-550	20-551	20-552	20-553	20-554	20-555	20-556	20-557	20-558	20-559	20-560	20-561	20-562	20-563	20-564	20-565	20-566	20-567	20-568	20-569	20-570	20-571	20-572	20-573	20-574	20-575	20-576	20-577	20-578	20-579	20-580	20-581	20-582	20-583	20-584	20-585	20-586	20-587	20-588	20-589	20-590	20-591	20-592	20-593	20-594	20-595	20-596	20-597	20-598	20-599	20-600	20-601	20-602	20-603	20-604	20-605	20-606	20-607	20-608	20-609	20-610	20-611	20-612	20-613	20-614	20-615	20-616	20-617	20-618	20-619	20-620	20-621	20-622	20-623	20-624	20-625	20-626	20-627	20-628	20-629	20-630	20-631	20-632	20-633	20-634	20-635	20-636	20-637	20-638	20-639	20-640	20-641	20-642	20-643	20-644	20-645	20-646	20-647	20-648	20-649	20-650	20-651	20-652	20-653	20-654	20-655	20-656	20-657	20-658	20-659	20-660	20-661	20-662	20-663	20-664	20-665	20-666	20-667	20-668	20-669	20-670	20-671	20-672	20-673	20-674	20-675	20-676	20-677	20-678	20-679	20-680	20-681	20-682	20-683	20-684	20-685	20-686	20-687	20-688	20-689	20-690	20-691	20-692	20-693	20-694	20-695	20-696	20-697	20-698	20-699	20-700	20-701	20-702	20-703	20-704	20-705	20-706	20-707	20-708	20-709	20-710	20-711	20-712	20-713	20-714	20-715	20-716	20-717	20-718	20-719	20-720	20-721	20-722	20-723	20-724	20-725	20-726	20-727	20-728	20-729	20-730	20-731	20-732	20-733	20-734	20-735	20-736	20-737	20-738	20-739	20-740	20-741	20-742	20-743	20-744	20-745	20-746	20-747	20-748	20-749	20-750	20-751	20-752	20-753	20-754	20-755	20-756	20-757	20-758	20-759	20-760	20-761	20-762	20-763	20-764	20-765	20-766	20-767	20-768	20-769	20-770	20-771	20-772	20-773	20-774	20-775	20-776	20-777	20-778	20-779	20-780	20-781	20-782	20-783	20-784	20-785	20-786	20-787	20-788	20-789	20-790	20-791	20-792	20-793	20-794	20-795	20-796	20-797	20-798	20-799	20-800	20-801	20-802	20-803	20-804	20-805	20-806	20-807	20-808	20-809	20-810	20-811	20-812	20-813	20-814	20-815	20-816	20-817	20-818	20-819	20-820	20-821	20-822	20-823	20-824	20-825	20-826	20-827	20-828	20-829	20-830	20-831	20-832	20-833	20-834	20-835	20-836	20-837	20-838	20-839	20-840	20-841	20-842	20-843	20-844	20-845	20-846	20-847	20-848	20-849	20-850	20-851	20-852	20-853	20-854	20-855	20-856	20-857	20-858	20-859	20-860	20-861	20-862	20-863	20-864	20-865	20-866	20-867	20-868	20-869	20-870	20-871	20-872	20-873	20-874	20-875	20-876	20-877	20-878	20-879	20-880	20-881	20-882	20-883	20-884	20-885	20-886	20-887	20-888	20-889	20-890	20-891	20-892	20-893	20-894	20-895	20-896	20-897	20-898	20-899	20-900	20-901	20-902	20-903	20-904	20-905	20-906	20-907	20-908	20-909	20-910	20-911	20-912	20-913	20-914	20-915	20-916	20-917	20-918	20-919	20-920	20-921	20-922	20-923	20-924	20-925	20-926	20-927	20-928	20-929	20-930	20-931	20-932	20-933	20-934	20-935	20-936	20-937	20-938	20-939	20-940	20-941	20-942	20-943	20-944	20-945	20-946	20-947	20-948	20-949	20-950	20-951	20-952	20-953	20-954	20-955	20-956	20-957	20-958	20-959	20-960	20-961	20-962	20-963	20-964	20-965	20-966	20-967	20-968	20-969	20-970	20-971	20-972	20-973	20-974	20-975	20-976	20-977	20-978	20-979	20-980	20-981	20-982	20-983	20-984	20-985	20-986	20-987	20-988	20-989	20-990	20-991	20-992	20-993	20-994	20-995	20-996	20-997	20-998	20-999	20-1000	20-1001	20-1002	20-1003	20-1004	20-1005	20-1006	20-1007	20-1008	20-1009	20-1010	20-1011	20-1012	20-1013	20-1014	20-1015	20-1016	20-1017	20-1018	20-1019	20-1020	20-1021	20-1022	20-1023	20-1024	20-1025	20-1026	20-1027	20-1028	20-1029	20-1030	20-1031	20-1032	20-1033	20-1034	20-1035	20-1036	20-1037	20-1038	20-1039	20-1040	20-1041	20-1042	20-1043	20-1044	20-1045	20-1046	20-1047	20-1048	20-1049	20-1050	20-1051	20-1052	20-1053	20-1054	20-1055	20-1056	20-1057	20-1058	20-1059	20-1060	20-1061	20-1062	20-1063	20-1064	20-1065	20-1066	20-1067	20-1068	20-1069	20-1070	20-1071	20-1072	20-1073	20-1074	20-1075	20-1076	20-1077	20-1078	20-1079	20-1080	20-1081	20-1082	20-1083	20-1084	20-1085	20-1086	20-1087	20-1088	20-1089	20-1090	20-1091	20-1092	20-1093	20-1094	20-1095	20-1096	20-1097	20-1098	20-1099	20-1100	20-1101	20-1102	20-1103	20-1104	20-1105	20-1106	20-1107	20-1108	20-1109	20-1110	20-1111	20-1112	20-1113	20-1114	20-1115	20-1116	20-1117	20-1118	20-1119	20-1120	20-1121	20-1122	20-1123	20-1124
----------------	------	------	------	------	------	------	------	------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------	---------

TABLE N6,6-III (CONTINUED)
NATIONAL EMISSIONS INVENTORY
NYLON 6,6 FROM NYLON SALT

NOTES

1. Composition + symbol means presence of compound as a trace.
2. Type of Analysis, symbols mean:

TIT - Titration
GC - Gas Chromatography
TOC - Total Organic Carbon
CRAV - Gravimetric Analysis

3. Particulates/Aerosols

Counts the following compounds: Hexamethylene Diamine, Adipic Acid, Nylon Salt, Nylon 6,6 Polymer, Cyclopentanone, Halide, Sulfonamide.

TABLE No. 6-IV
CATALOG OF EMISSION CONTROL DEVICES
NYLON 6,6

Absorber/Scrubber	20-3	20-2
EPA Code	(E)	(b)
Flow Diagram Stream I, D.		
Device I, D. No.		
Control Emission of		
Scrubbing/Absorbing Liquid		
Type		
Scrubbing/Absorbing Liquid Rate GPM		
Design Temp. (Operating Temp.) °F		
Gas Rate SCFH (lb./hr.)		
T-T Height - Feet		
Diameter - Feet		
Washed Gases to Stack		
Stack Height - Feet		
Stack Diameter - Feet		
Installed Cost, Mat'l. & Labor - \$		
Installed Cost Based on - "year" - dollars		
Operating Cost - c/lb. Nylon 6,6/Yr.		
Value of Recovered Product, \$/Yr.		
Net Operating Cost, c/lb. Nylon 6,6		
Efficiency - % - SE		
Efficiency - % - SERR		
	15	Hexamethylene Diamine
	(100° F)	Water
	(40)	Spray Column
	89,000	
	1968	
	0.071	
	19,850	
	0	
	0.016	
	99.7	
	99.7	

*Details not available - equipment in process of being designed for addition in near future.

TABLE No. 6-V
NUMBER OF NEW PLANTS BY 1980

Current Installed Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand* 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
1,523	0	1,523	2,400	3,000	1,477	150	10

Notes:

1. All capacities in MM lbs./year (million lbs./year).
2. Demand estimated at 80% of installed capacity.
3. Growth rate of 10%/year assumed.

TABLE N6, 6-VI
EMISSION SOURCE SUMMARY
TON/TON NYLON 6, 6

Emission	Source					Total
	Evaporation Section	Reactor Section	Flasher Section	Finishing	Fugitive	
Hydrocarbons	0	0	0	0	0	0
Particulates & Aerosols	0.000333	0.002100	0.001100	0.000044	0	0.003577
NO _x	0	0	0	0	0	0
SO _x	0	0	0	0	0	0
CO	0	0	0	0	0	0

TABLE No. 6-VII
WEIGHTED EMISSION RATES

Chemical	Nylon 6, 6	Process	Batch and Continuous Polymerization	Increased Capacity by 1980	1,480 MM Lbs./Year	Emissions, lb./lb. Nylon 6, 6	Increased Emissions MM lbs./year	Weighting Factor	Weighted Emissions MM lbs./year
Pollutant									
Hydrocarbons	0					0	0	80	0
Particulates & Aerosols	0.003577					5.294		60	317.6
NO _x	0					0	0	40	0
SO _x	0					0	0	20	0
CO	0					0	0	1	0

Significant Emission Index = 318

Oxo Process

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	OA-1
II. Process Description	OA-2
III. Plant Emissions	OA-4
IV. Emission Control	OA-6
V. Significance of Pollution	OA-7
VI. Oxo Alcohol Producers	OA-8

List of Illustrations and Tables

Flow Diagram	Drawing R-229
Net Material Balance	Table OA-I
Gross Heat Balance	Table OA-II
Emission Inventory	Table OA-III
Catalog of Emission Control Devices	Table OA-IV
Number of New Plants by 1980	Table OA-V
Emission Source Summary	Table OA-VI
Weighted Emission Rates	Table OA-VII

I. Introduction

One of the processes which gained world wide importance during recent years is the so called Oxo synthesis for the production of aldehydes and alcohols from olefins and synthesis gas ($\text{CO} + \text{H}_2$). Although the oxo synthesis or hydroformylation was discovered in 1938, the big industrial success has been only recently - within the last 15 to 20 years.

In terms of production capacity the oxo process (combined with an aldol condensation to double molecular weight) is the largest process for producing alcohols from the butanols (C_4) up through the hexadecanols (C_{16}) and higher.

Hydrocarbons and particulates are the main air pollutants associated with these plants. To a lesser degree, CO is a problem but a very minor one. The main odor problem appears to be trace quantities of aldehydes and alcohols in vents from distillation columns and tanks. Unfortunately, even trace quantities of these compounds are enough to create a local odor problem in the plant. Particulates arise from loss of catalyst (metallic oxides) from the system in vent gases but these losses are very small and constitute no apparent problem. Off-gases from the process consist of CO , H_2 and hydrocarbons, chiefly C_1 to C_4 paraffins. These gases are either flared or sent to refinery fuel gas. In either event, proper combustion should give CO_2 and water. (1) Combustion efficiencies are estimated at 98 to 100 percent and CO and hydrocarbon release to the air is under control almost all of the time.

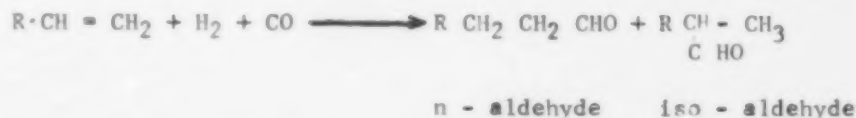
Current oxo alcohol production is about 1727 million lbs./year. Assuming a growth of 8 - 9 percent per year, an installed capacity of 3000 million lbs. is predicted by 1980 which will be equal to the demand by then. This is based on current use of plasticizers in PVC plastics and as bases for surfactants. Both these uses should increase up through 1980.

(1) Although the flaring will produce small quantities of NO_x .

II. Process Description

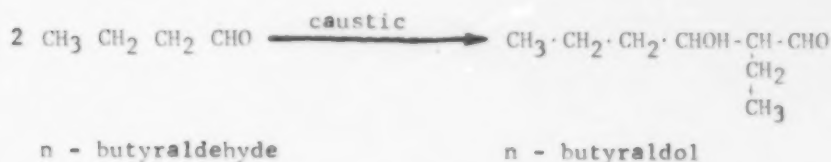
The oxo process is the commercial application of a chemical reaction called oxonation or, more properly, hydroformylation. In this reaction, hydrogen and carbon monoxide are added across an olefinic bond (C=C) to produce aldehydes containing one more carbon atom than the olefin. Several reactions are involved but for simplicity, we shall mention only the three basic reactions taking place.

- (1) Hydroformylation of an olefin to an aldehyde (Oxo Process).



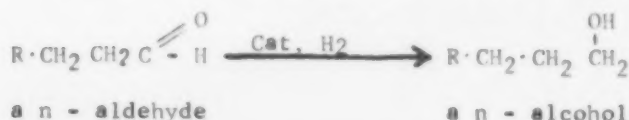
The straight chain n - aldehyde is the preferred product.

- (2) Aldol Condensation - Doubling of the molecular weight of an aldehyde.
Example - n - butyraldehyde.



The n - butyraldol may be dehydrated and hydrogenated to an alcohol, 2 ethyl hexanol.

- (3) Hydrogenation of the aldehydes to the corresponding alcohol.



In commercial practice all three of these reactions are used individually or in common as follows:

Oxo Process

The reaction of an olefin (propylene, octenes, etc.) with carbon monoxide and hydrogen (syn gas made by steam reforming of methane, ethane, etc.) at 200 - 400° F and 500 - 5000 PSI pressure, in the presence of a cobalt catalyst produces a mixture of aldehydes and alcohols with one more carbon atom than the starting olefin. This reaction is properly known as oxonation (hence "oxo") or more accurately, hydroformylation. Following removal of the catalyst (decobalting) the reaction mixture is catalytically hydrogenated. The resulting product is then fractionated to yield the finished "oxo" alcohol. Except when ethylene is used as the starting olefin, a mixture of straight chain and branched chain alcohols are produced. With propylene and higher molecular weight linear olefins, the percentage of normal alcohol product can be significantly increased by modifying the cobalt catalyst system, e.g. with phosphine ligands. All alcohols produced by this technique are primary, regardless of the feedstock used.

Aldol Process

N - butyraldehyde in the presence of caustic condenses to form 2 - ethyl hexenal which on hydrogenation and distillation yields pure 2 - ethyl - 1 - hexanol (2 EH). This alcohol was the first large volume synthetically produced higher aliphatic primary alcohol and is still today the most important member of the group. N - butyraldehyde may be made by subjecting propylene to the oxo reaction. The aldol condensation doubles the number of carbon atoms in the alcohol precursor made in the oxo reaction.

Oxo Aldol (Combined) Process

In the combined process, with propylene as the feedstock and a special catalyst system, 2 - ethyl hexanol is produced via the oxo - aldol route in one operation. One of the special catalyst systems is a tributyl phosphine cobalt carbonyl complex (plus KOH) which promotes a high degree of linearity of the intermediate butyraldehyde and hence high yields of 2 - ethyl hexanol. Branched chain hexadecyl alcohol is also made by a combined oxo - aldol process. In this case branched chain heptenes are the feedstock and the cobalt catalyst is modified by the addition of metal organic compounds such as zinc, cadmium or lead stearates.

Plants covered by this report include plain oxo plants with subsequent hydrogenation to alcohols and plants with oxo - aldol routes to higher molecular weight alcohols.

III. Plant Emissions

No two oxo alcohol plants are exactly alike or even closely alike. The comments below refer to the generalized flow diagram OA-1 in this report which gives all the basic steps which most of these plants possess.

A. Continuous Air Emissions

1. Reforming Furnaces Vent Gas (A)

Some respondents gave data on operation of their steam reforming furnaces (to CO + H₂ "syn gas") and hydrogen production facilities. Emissions from this source represent emergency flarings of gases due to upsets. The figures given are probably low since all plants have these furnaces but data was not given for all plants.

2. Oxo Reactor System Off-Gas (C)

All plants have a reactor system off-gas which is normally flared. Usual composition is steam, N₂, CO, H₂ and light hydrocarbons. Gases are burned to CO₂ and H₂O with better than 98% efficiency. Some hydrocarbons and CO may escape unburned and these are shown on Table III. One respondent had a measure of the small quantity of NO_x found in the flare gas from N₂ present in the combustion air. Very small quantities of particulates (catalyst - metallic oxides) were reported in several streams and this has been noted also on Table III.

3. Catalyst System Vent Gas (D), (E)

Chief emission here is water as steam but small quantities of hydrocarbons are reported (aldehydes, alcohols) and these represent a minor in-plant odor problem. Also trace quantities of particulates (catalyst - metal oxide) are present in this stream.

4. Compressor Engine Exhaust

One respondent uses methane fueled engines to drive his compressors which are used to feed syn gas and hydrogen to the process. Since all the plants using the oxo process are pressure plants (1500 - 6500 PSIG) in the reaction section, they all must have compressors. Others may be methane or gas fueled also but were not reported. Since engine exhaust is a pollutant, we reported this source. Even though it is small, it is an inherent part of the process. The figure shown is probably low since other plants may well have gas fueled engines on their compressors also.

5. Distillation Purification System Vents (F), (I)

Gases here are chiefly steam and hydrocarbon (aldehyde and alcohol in this case) and represent a local odor problem.

6. Heavy Liquids Incinerator Stack Gas (L), (H)

Some plants burn the heavy by-products made in an incinerator. others send them to disposal in refinery fuel oil where we have no

data. Those incinerating this stream report practically complete combustion but in every case trace amounts of aldehydes and alcohols can be detected in the stack gas. This stream also represents a local odor problem.

Many of the respondents have only one or two emissions listed. Other vent streams go into the refinery fuel system and are not counted as emissions in this report. One respondent (21-3) reports no emissions at all - everything being sent to the refinery fuel system. One cannot help but wonder that there must be some emergency venting to a flare or the atmosphere in this plant too - every other plant reports some of this but no emission data were forthcoming from 21-3. Nevertheless, this plant was averaged in with all the others and in effect diluted the emissions shown in Table III because of the claimed 100% purity.

B. Intermittent Air Emissions (see A-1)

Some plants vent the reforming furnaces continuously and some report only intermittent emissions due to upsets or start-up.

C. Continuous Liquid Wastes (L), (M)

All plants have liquid waste consisting of heavy organics which are incinerated, burned in refinery fuel, or reprocessed. (See Section A-6.)

Waste Water (J)

Every plant has a waste water stream which varies from 0.06 gal/lb. product to 1.7 gal/lb. product. Five of seven respondents treat this water at least thru primary treatment. The remaining two have no treatment other than oil skimming.

D. Solid Wastes (K)

Five of seven respondents report periodic removal of solid wastes from the process in the form of spent catalyst. They are disposed of by landfill in the plant or sold to an outside firm for reclamation. Amounts vary from 0.000053 lb./lb. product to 0.001680 lb./lb. product but the data is sketchy.

E. Odors

Some respondents reported the odor of heavy aldehydes and alcohols in plant but no one reported any outside odor complaints. As stated earlier, these compounds have odors enduring enough that they could probably be detected off-site if the wind and atmospheric conditions were right.

F. Fugitive Emissions

None of the respondents report any fugitive emissions or even offer an estimate.

G. Other Emissions

None reported.

IV. Emission Control

Emission control devices used in this process are summarized in Table IV. All plants have flares which are used to burn excess gas or gases emitted due to process upset or start-up. In all cases, using the data reported, combustion efficiency is better than 98% and all components could burn completely to CO_2 and H_2O . No nitrogen compounds are present although traces of NO_x have been reported in the flared gas, presumably from N_2 present in small quantities in the syn gas and from the air required for complete combustion in the flare. No sulfur compounds are used in these plants. Emissions to the air, when they occur, are hydrocarbons (chiefly $\text{C}_1 - \text{C}_4$ aliphatics), particulate and CO and take place generally during an upset or start-up with the resultant surge of feed to the flare.

Heavy residual liquids are incinerated and the only source of emissions here are trace quantities of heavy aldehydes and alcohols which are detectable by their odor in the stack gas. This source represents a minor local odor problem at the plants.

One respondent has a water scrubber on his aldehyde and alcohol column vents to attempt to reduce the odor of gases emitted. The scrubbed gases still present an odor problem although the aldehyde and alcohol content can only be reported as "trace". The major constituent is air. Since actual quantitative data are not available for the flared and incinerated gases, a Completeness of Combustion Rating ("CCR") and Significance of Emission Reduction Rating ("SERR") cannot be calculated. From the sparse and incomplete data available, however, we estimate a 98+% for both these ratings and generally rather close to 100%.

The one water scrubber used removes trace quantities of aldehydes and alcohols from distillation column vent gases. Since the odor of aldehydes and alcohols is still detectable in the scrubbed off-gas, one must conclude that the efficiency of this device is not 100% but a lesser figure. Lack of quantitative data precludes calculation of an exact efficiency.

V. Significance of Pollution

It is recommended that no in-depth study of this process be made. Reported emissions on a weighted basis (Table VII, SEI = 325) put the plants on the lower end of the emission spectrum. It should be mentioned that several plants reported a local in-plant odor problem with heavy alcohols and aldehydes in storage tank breathers and distillation column vents. Although no odor complaints were reported, these odors are tenacious enough that they probably could be detected off-site if the wind were in the proper direction.

Methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from new plants. This work is summarized in Tables V, VI and VII.

The projected increase in oxo alcohol production has been estimated from literature comments on possible future uses. Published support for this forecast has not been found. Assumptions made were:

1. A major use of $C_6 - C_{12}$ alcohols will continue to be as bases for plasticizers for polyvinyl chloride plastics. PVC plastics are projected to grow 9 - 12 percent per year through 1980.
2. A major use of $C_{12} - C_{18}$ alcohols will be as bases for surfactants and this market is projected to grow also.
3. No more natural fatty alcohol plants will be built.
4. The recent oversupply of oxo alcohols has now been alleviated by increased demand. Supply and demand will be about equal in 1980.

Using the above assumptions, it was projected that the oxo alcohol market will increase from 1,727 million lbs./year to about 3,000 million lbs by 1980. One marginal oxo unit has already been shut down. All the others apparently will keep on running until at least 1980. New plants (six required) will have a capacity averaging 200 million lbs./year. On a weighted emission basis, an SEI of 325 was calculated for this project and as such it is recommended that no in-depth study be made.

VI. Producers of Oxo Alcohols

The capacities and plant locations listed below are based on information provided in the questionnaires and in the literature.

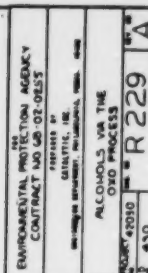
<u>Company</u>	<u>Location</u>	<u>Capacity MM Lbs./Yr.</u>	<u>Type*</u>
Dow Badische	Freeport, Texas	180	i & n C ₄ , i & n butal, 2 EH
Eastman Kodak, Eastman Chem. Prod.	Longview, Texas	435	i & n C ₄ , i & n butal, 2 EH, prop. ald.
Getty Oil	Del. City, Del.	42	i C ₈ , i C ₁₀ , i C ₁₃
Gulf Oil	Phila. Pa.	40	i C ₁₃
Monsanto	Texas City, Texas	200	n - C ₇ , C ₉ , C ₁₁
Shell	Deer Park, Texas	150	i & n C ₄ , i & n butal, 2 EH
	Geismar, La.	150	n - C ₁₂ , C ₁₃ , C ₁₄ , C ₁₅
Exxon Corp.	Baton Rouge, La.	160	i - C ₈ , C ₉ , C ₁₀ C ₁₃ , C ₁₆
Union Carbide Corp.	Seadrift, Texas	100	i & n C ₄ , n - butal i C ₆ , C ₈ , C ₁₀ , C ₁₃ prop. ald.
	Texas City, Texas	200	Same as Seadrift plant & n C ₃ & C ₅
U. S. Steel	Haverhill, Ohio	<u>70</u>	i - C ₈ - C ₁₀

Total = 1,727 million lbs/year

*Key to type of alcohol

i & n C₄ = iso & normal butyl alcohol
 i C₆ = iso hexyl alcohol
 i C₈ etc. = iso octyl alcohol

 i & n butal = iso & normal butyraldehyde
 2 EH = 2 ethyl - 1-hexanol
 n C₆ - C₁₁ = normal C₆ to C₁₁ alcohols (linear)
 prop - ald. = normal propionaldehyde



NOTE
1) DOTTED LINES SHOW STEPS
WHICH ARE OPTIONAL

TABLE QA-1
ALCOHOLS FROM THE OXO PROCESS
MATERIAL BALANCE - T/T ALCOHOL

There are insufficient data for a good material balance on this complex process. A partial balance can be made on olefins charged to the process vs alcohol made. Data given below do not account for either syn. gas ($\text{CO} + \text{H}_2$) charged or gaseous products leaving the process.

1.578 lb. olefin (1) -----	1.000 lb. alcohol (2)
	0.264 light oxo "gasoline"
	0.133 heavy liquid ends
	0.181 light ends (gas) (3)

It should be noted that this is an "average" balance and does not apply to any individual product or grade of products.

-
- (1) C_3 to C_{12} .
 (2) C_4 to C_{16} .
 (3) By difference.

TABLE OA-II
ALCOHOLS VIA THE OXO PROCESS
REACTOR HEAT BALANCE

There are not sufficient data available to permit the construction of a detailed heat balance for this complex series of reactions. The literature lists the following:

- (1) The reaction is highly exothermic once initiated.
- (2) The reaction is first order relative to the olefin charge.
- (3) Heat release.
 - (a) 50,000 BTU/lb. mol olefin converted to alcohol.
 - (b) 62,500 BTU/lb. mol ethylene converted to alcohol
 - (c) Ethylene $\longrightarrow$ propionaldehyde + 34.8 kcal./mol released.

TABLE OA-III
NATIONAL EMISSIONS INVENTORY
ALCOHOLS BY THE OXO PROCESS

Page 1 of 4

Plant EPA Code No. Capacity - Tons Alcohols/Year Range of Production - % of Max. Emissions to Atmosphere Stream	21-1 90,000 0	21-2 75,000 0	21-3 75,000 0
	Ald., Alc., Heavy Liquids to Incinerator	Ald., Alc., Heavy Liquids to Incinerator	Ald., Alc., Heavy Liquids to Incinerator
Flow - Lbs./Hr. (SCFM) Flow Characteristic If Intermittent Composition - Ton/Ton Alc.	9879 Continuous (a)	3112 Continuous (a)	3112 Continuous (a)
Hydrogen Nitrogen (Air) CO CO ₂ Steam NO _x	0.01113 0.28483 0.13356 Trace	0.00006 0.00044 0.15268 0.01092 0.00006	0.00003 0.00118 0.14054 0.02002 0.00076
C ₁ - C ₆ & Higher Hydrocarbons Aldehydes & Alcohols Particulates	Trace	Trace	Trace
Vent Stacks Number Height - Feet Diameter, Inches Exit Gas Temp. °F SCFM/Stack Emission Control Devices	1 18 60 ? Incinerator	1 20 4 100° 470 None	1 100 14 1000° 228 Flare
Analysis Date or Frequency of Sampling Tap Location Type Analysis Odor Problem Summary of Air Pollutants Hydrocarbons - Ton/Ton Alc. Aerosols - Ton/Ton Alc. NO _x - Ton/Ton Alc. SO _x - Ton/Ton Alc. CO - Ton/Ton Alc.	Never Estimate No Trace 0.07609	Never Estimate Yes Incinerator	Never Estimate No 0.02090 0.00050

TABLE DA-III
NATIONAL EMISSIONS INVENTORY
ALCOHOLS BY THE OXO PROCESS

Page 2 of 4

Plant EPA Code No. Capacity - Tons Alcohols/Year Range of Production - % of Max. Emissions to Atmosphere Stream	21-4 48,000 0	21-5 217,500 0	21-6 35,000 0
Flow - Lbs./Hr. (SCFM) Flow Characteristic If Intermittent, Hrs./Yr. Composition - Ton/Ton Alc. Hydrogen Nitrogen (Air) CO CO ₂ Steam NO _x C ₁ - C ₆ & Higher Hydrocarbons Aldehydes & Alcohols Particulates Vent Stacks Number Height - Feet Diameter - Inches Exit Gas Temp. of SCFM/Stack Emission Control Devices	Oxo Reactor Vent Gas 119.02% Continuous (b) 6.9287 3.8915 0.00027 0.00002 1 120 Flare Never Est. from Feed No 0.00002 0.00027	Oxo Reactor Vent Gas 2072 Continuous (b) 0.00002 0.00026 0.00030 0.02827 0.01287 Trace 1 100 20 Flare 12/day in-line G. C. No 0.00024 Trace 0.00030	Oxo Reactor Vent Gas 18,240 Continuous (b) 0.02589 1.7295 0.95710 1 125 16 213 ^o 360,000 Flare Once in-line G. C. No

Plant EPA Code No.
Capacity - Tons Alcohols/Year
Range of Production - % of Max.
Emissions to Atmosphere
Stream

Flow - Lbs./hr. (SCFM)
Flow Characteristic
if Intermittent, hrs./Yr.
Composition - Ton/Ton Alc.
Hydrogen
Nitrogen (Air)
CO
CO₂
Steam
NO_x
C₁ - C₄ & Higher Hydrocarbons
Aldehydes & Alcohols
Particulates

Vent Stacks

Number
Height - Feet
Diameter - Inches
Exit Gas Temp. °F
SCFM/Stack
Emission Control Devices

Analysis

Date or Frequency of Sampling
Tap Location
Type of Analysis
Odor Problem
Summary of Air Pollutants
Hydrocarbons - Ton/Ton Alc.
Aerosols - Ton/Ton Alc.
NO_x - Ton/Ton Alc.
SO_x - Ton/Ton Alc.
CO - Ton/Ton Alc.

TABLE QA-III
NATIONAL EMISSIONS INVENTORY
ALCOHOLS BY THE OXO PROCESS

Page 3 of 4

		21-7			
		80,000			
		0			
Hyd. Reformer Vent	CO ₂ Removal Vent	Cat. Recovery System Vent	Cat. Regenerator System Vent		
(7 Avg.) Intermittent 8	302 Continuous	730 Continuous	19 Continuous		
0.000032	0.000063	0.022260	0.00058		
0.000002	0.009404				
0.000178					
0.000577					
0.000006					
2	1	Trace	Trace		
		1	1		
	42	151	4		
None	None	None	None		
Never	Once	Never	Never		
Estimate	In-line	Calculated	Calculated		
No	G.C.	Yes	Yes		
	No				

TABLE OA-III
NATIONAL EMISSIONS INVENTORY
ALCOHOLS BY THE OXO PROCESS

Page 4 of 4

Plant EPA Code No. Capacity - Tons Alcohols/Year Range of Production - % of Max. Emissions to Atmosphere Stream	21-7 80,000 0	Distn. Column Vent 110 Continuous	Storage Tank Vents 96 Continuous	Oxo Reactor Vent Gas, Etc. 3544 Continuous (b) 0.000113 0.017857 0.000940 0.53571 0.038496
Flow - Lbs./Hr. (SCFM) Flow Characteristic if Intermittent, Hrs./Yr. Composition - Ton/Ton Alc.	Compressor Flush Lines (0.01 Avg.) Intermittent 1	Trace Trace Trace Trace	Trace	
Hydrogen Nitrogen (Air) CO CO ₂ Steam NO _x	Trace Trace Trace Trace	Trace Trace Trace Trace	Trace	
C ₁ - C ₄ & Higher Hydrocarbons Aldehydes & Alcohols Particulates Vent Stacks	Trace Trace	Trace	Trace	
Number Height - Feet Diameter - Inches Exit Gas Temp. °F SCFM/Stack Emission Control Devices	3 None	1 35 None	1 None	1 200 24 ? 606 Flare
Analysis Date or Frequency of Sampling Tap Location Type of Analysis Odor Problem Summary of Air Pollutants Hydrocarbons - Ton/Ton Alc. Aerosols - Ton/Ton Alc. NO _x - Ton/Ton Alc. SO _x - Ton/Ton Alc. CO - Ton/Ton Alc.	Never No	Never Calculated No	Never Calculated No	3 times/year line to flare M.S. No 0.000066 0.000942

EXPLANATION OF NOTES
TABLE QA-III
NATIONAL EMISSIONS INVENTORY
ALCOHOLS VIA THE OXO PROCESS

- (a) Respondents furnished composition of liquid to incinerator. Figures shown are calculated combustion products assuming complete combustion to CO_2 and water unless other data were available. Usually trace quantities of alcohols, aldehydes or particulates were noted in the incinerator stack gases and usually there is a minor odor problem associated with these incinerators.
- (b) Respondents furnished composition of gas streams to the flare. Figures shown are calculated on 98% complete combustion to CO_2 and H_2O unless other data were available. In most cases, some pollutants appear to be in the flared gas but they were so low that no odor problem was reported. Small quantities of NO_x are present in the flared gas from N_2 in the combustion air.
- Type of Analysis M.S. = Mass Spectrograph
 G.C. = Gas Chromatograph
 TOC = Total Organic Carbon
 TIT = Titration
- (c) Plant 21-1 gives large volume of methane as fuel to gas compressors. Compressor exhaust estimated by an arbitrary choice of 50% CH_4 going to CO_2 and 50% to CO in the engines.

Many plants vent gas streams to refinery fuel systems and use the flare only in cases of upset or emergency. Hence, some plants listed show no flared gas at all or low flow to the flare. One respondent showed all gas streams going to plant fuel line and no atmospheric emissions at all. This appears overly optimistic and this data was taken with a grain of salt.

TABLE OA-IV
CATALOG OF EMISSION CONTROL DEVICES
ALCOHOLS VIA THE OXO PROCESS

Page 1 of 3

INCINERATION DEVICES

EPA Code No. for plant using Flow Diagram (Fig. 1) Stream I, D.	Device I, D. No.	Type of Compound Incinerated	Material Incinerated, Lb./Hr. (SCFM)	Auxiliary Fuel Req'd. (excl. pilot)	Type	Rate - BTU/Hr.	Device or Stack Height - Feet	Installed Cost - Mat'l. & Labor - \$	Installed Cost Based on "Year" - \$	Installed Cost - c/lb. Alcohol - Yr.	Operating Cost - Annual (1972) - \$/Yr.	Efficiency - % - CCR	Efficiency - % - SERR
21-1 (L) (H)	101	Heavy Alcohols & Aldehydes & Misc. Waste Liquid Incinerator	2350			18	\$12,700	1967 - 1972	0.0071	\$5,800	0.0032	Approximately 99%	Approximately 99%
21-1 (C)	102	Syn. Gas & Hydrocarbons Flare	1019			75	\$10,365	ca. 1967	0.0058	\$5,600	0.0031	100 (1)	100 (1)
21-2 (A) (C)	101	Syn. Gas & Hydrocarbons Flare	38			5.5 x 10 ⁶	100	\$145,000	1941 to 1972	0.0947	\$40,000	66 - 100 (2)	15 - 100 (2)
21-2 (A) (C)	101	Syn. Gas & Hydrocarbons Flare	38			5.5 x 10 ⁶	100	\$145,000	1941 to 1972	0.0947	\$40,000	66 - 100 (2)	15 - 100 (2)

INCINERATION DEVICES

EPA Code No. for plant using Flow Diagram (Fig. 1) Stream I, D.	Device I, D. No.	Type of Compound Incinerated	Material Incinerated, Lb./Hr. (SCFM)	Auxiliary Fuel Req'd. (excl. pilot)	Type	Rate - BTU/Hr.	Device or Stack Height - Feet	Installed Cost - Mat'l. & Labor - \$	Installed Cost Based on "Year" - \$	Installed Cost - c/lb. Alcohol - Yr.	Operating Cost - Annual (1972) - \$/Yr.	Efficiency - % - CCR	Efficiency - % - SERR
21-2 (L) (H)	102	Butanol, Butyl Ether, Heavy Ends, Cat. Salts Incinerator	1920			10 x 10 ⁶	?	\$155,000	1959 - 1970	0.1033	\$51,200	0.034	Approximately 99%
21-4 (A) (C)	101	Syn. Gas & Hydrocarbons Flare	35281			120	\$9,077 (3)	1971 - 1972	0.00946	\$20,284	0.02113	100 (1)	100 (1)
21-5 (A) (C)	101	Syn. Gas & Hydrocarbons Flare	754			100	\$97,000	1948 - 1949	0.0223	\$16,000	0.00348	98 (1)	98 (1)

(1) So reported by respondent.

(2) Worst case based on no burning of hydrocarbons during up-sets. Best case assumes all go to CO₂ & H₂O actual performance lies between these extremes, not enough data to pin down any closer.

(3) Tip only and steam line on existing flare tower.

TABLE 1A-IV
CATALOG OF EMISSION CONTROL DEVICES
ALCOHOLS VIA THE OXO PROCESS

Page 2 of 3

INCINERATION DEVICES

EPA Code No. for plant using
Flow Diagram (Fig. 1) Stream I, D.
Device I, D. No.
Type of Compound Incinerated
Type of Device
Material Incinerated, lb./hr. (SCFH)
Auxiliary Fuel Req'd. (excl. pilot)
Type
Rate - BTU/hr.
Device or Stack Height - Feet
Installed Cost - Mat'l. & Labor - \$
Installed Cost Based on "Year" - \$
Installed Cost - c/lb. Alcohol - Yr.
Operating Cost - Annual (1972) - \$/Yr.
Operating Cost - c/lb. Alcohol
Efficiency - % - OCH
Efficiency - % - SERE

21-6
(A) (C)
101
Syn. Gas
Flare
(6000)

21-7
(A) (C)
101
Syn. Gas & Hydrocarbons
Flare
631

125
550,000
1962
0.0714
\$4,220
0.00603
100 (1)
100 (1)

200
\$245,000
1966
0.1531
\$61,500
0.0384
Approximately 98
Approximately 98

- (1) So reported by respondent.
- (2) Worst case based on no burning of hydrocarbons during up-sets. Best case assumes all go to CO₂ & H₂O actual performance lies between these extremes, not enough data to pin down any closer.
- (3) Tip only and steam line on existing flare tower.

ABSORBERS/SCRUBBERS

EPA Code No. for plant using
Flow Diagram (Fig. I) Stream I, D.
Device I, D, No.
Controls Emission of
Scrubbing/Absorbing Liquid
Type
Scrubbing/Absorbing Liquid Rate GPM
Gas Rate - SCFM (lb./hr.)
T-I Height, Feet
Diameter, Feet
Washed Gases to Stack
Stack Height - Feet
Stack Diameter - Inches
Installed Cost - Mat'l. & Labor - \$
Installed Cost - Based on "Year" - \$
Installed Cost - c/lb. Alcohol/Yr.
Operating Cost - Annual - \$ (1972)
Value of Recovered Product, \$/Yr.
Net Operating Cost - c/lb. Alcohol
Efficiency - % - SE
Efficiency - % - SERR

TABLE QA-IV
CATALOG OF EMISSION CONTROL DEVICES
ALCOHOLS VIA THE OXO PROCESS

21-1	
(F) (I)	
103	
Alcohol & Aldehyde Vapors	
Water	
Scrubber	
2	
?	
7.5	
1.5	
?	
15	
3	
\$1,680	
1967 - 1972	
0.00093	
\$3,600	
0	
0.0020	
<100	
<100	

TABLE QA-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity* 1980	Capacity to be Added	Economic Plant Size	Number of New Units
1727	0	1727	3000	3000	1273	200	6

NOTE: All capacities in million lbs./year.

*Based on use of alcohols as plasticizers in PVC and detergents and assuming that no new natural fatty alcohol plants will be built. Current over capacity of oxo alcohols should be over well before 1980 and new plants or expansion of existing facilities necessary to meet a growth rate of 8.9%/year.

TABLE QA-VI
EMISSION SOURCE SUMMARY
TON/TON ALCOHOL

Emission	Source						Total
	Reforming Furnaces Vent Gas	Oxo Reactor System Off-Gas	Catalyst System Vent Gas	Compressor Engine Exhausts	Distillation Purification System Vents	Heavy Liquid Incinerator Stack Gas	
Hydrocarbons	0.000009	0.000010	0.000040		0.002970	TR	0.003029
Particulates/aerosols		0.000003	TR			TR	0.000003
NO _x		0.000040					0.000040
SO _x							
CO	0.000009	0.000240		0.011000			0.011249

TABLE QA-VII
WEIGHTED EMISSION RATES

Chemical	Alcohols				
Process	Oxo				
Increased Capacity by 1980 1273 MM lbs./year					
Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year	
Hydrocarbons	0.003029	3.856	80	308.5	
Particulates	0.000003	0.0038	60	0.3	
NO _x	0.000040	0.0509	40	2.0	
SO _x			20	0	
CO	0.011249	14.320	1	14.3	
				14.3	
				Significant Emission Index = 325.1	

Phenol

Table of Contents

<u>Section</u>	<u>Page Numbers</u>
I. Introduction	PH-1
II. Process Description	PH-2
III. Plant Emissions	PH-3
IV. Emission Control	PH-7
V. Significance of Pollution	PH-10
VI. Phenol Producers	PH-11

List of Illustrations and Tables

Block Flow Diagram, Phenol from Cumene	Figure PH-1
Simplified Flow Diagram Phenol from Cumene	Figure PH-2
Basic Chemical Reactions	Table PH-I
Net Material Balance	Table PH-II
Cross Heat Balance	Table PH-II-A
Emission Inventory	Table PH-III
Catalog of Emission Control Devices	Table PH-IV
Number of New Plants by 1980	Table PH-V
Emission Source Summary	Table PH-VI
Weighted Emission Rates	Table PH-VII
References	Table PH-VIII

I. Introduction

Half the phenol produced goes into phenolic resins, while a substantial proportion is used to make the nylon-6 intermediate caprolactam. Natural phenol capacity accounts for only 2% of present day production, and the cumene process has replaced other synthetic phenol processes to such an extent that over 90% of U. S. capacity involves the use of cumene charge stock today.

In common with other air oxidation processes, venting of "spent air" accounts for a major portion of the emissions from the cumene derivation phenol process. In addition, since acetone is a major by-product, there is a roughly equivalent quantity of primarily low molecular weight hydrocarbon emissions associated with the product recovery and purification sections of the plant. Emissions of phenolic material is low, in keeping with the recognized toxicity of these materials, though respondents have noted phenolic odors are detectable at times, usually only within the plant. In general, air pollutant emissions from these phenol plants can be characterized as low to moderate.

This air pollution study report includes information provided by eight of the ten cumene process producers in the United States. According to Chemical Marketing Reporters' June 19, 1972 Chemical Profile, only three plants with a total capacity of 310 million pounds annually continue to produce phenol using other than the cumene process. Current cumene process capacity is approximately 2.5 billion pounds of phenol per year and is expected to increase to some 4.2 billion pounds per year by 1980.

No change in emission rate (i.e., tons emission/ton phenol) is foreseen except that, based on indications from respondents utilizing activated carbon for recovery of cumene from vented "spent air", other producers may find such pollution control equipment economically justified, and average hydrocarbon rate of emissions will actually be less in the future.

II. Process Description

The cumene process was developed by Hercules, and Distillers, Ltd. of England and concurrently, independently by Allied Chemical Corporation. First commercial production began in the early 1950's, with the cumene route taking over 50% of the market by 1968 and roughly 90% at the present time.

There are essentially two steps in the liquid phase production of phenol from cumene (see Table I and Figures PH-1 and PH-2). (i, ii, iii, iv, v ref.).

1. Air is introduced to a vigorously stirred, slightly alkaline aqueous sodium carbonate emulsion with purified cumene to produce cumene hydroperoxide (CHP).
2. Dilute sulfuric acid is added to a second agitated reactor to effect cleavage of the cumene hydroperoxide directly into phenol and acetone.

In the oxidation step, oil-soluble heavy metal catalyst and promoters may be present, and an emulsifying agent such as sodium stearate may be used. With a sodium carbonate solution pH in the range 8.5 to 10.5, and water-to-oil ratio between 2 and 5, reaction is carried out using about 0.5 pounds of oxygen per pound of phenol, and cumene recycle ratio of ~2:1, at temperatures up to 260° F and atmospheric or moderate superatmospheric pressure. Cooling is required (see Table II-A) to avoid thermal decomposition of the cumene hydroperoxide, and with conversion maintained in the range of 30 to 50%, "spent air" is vented through an effective refrigerated condensing system and other equipment for recovery and recycle of unconverted cumene. During this oxidation step, some formaldehyde is produced (along with some lesser quantities of other reaction products), indicating that the minor by-product acetophenone is also being formed.

Some producers elect to use a vacuum concentrator on the oxidation reactor effluent at this point, and to recycle separated overhead cumene to the oxidizer. In any case, precautions must be taken to avoid explosive concentrations of peroxides.

The cleavage step, which follows, involves intimate contact with dilute sulfuric acid (~5 - 25%) at temperatures in the range of 130 to 150° F and pressure slightly above atmospheric. Considerable heat is generated, and again it is important to provide adequate cooling to avoid thermal decomposition. There are undoubtedly a number of minor side reactions which occur in the cleavage reactor; it appears likely that the small amount of alpha methyl styrene produced results from loss of oxygen from CHP to form cumyl alcohol, followed by dehydration of the alcohol in the presence of sulfuric acid (see reactions III (A) and III (B) in Table I).

An aqueous acid phase from the cleavage reaction effluent separation is recycled back to the cleavage reactors with makeup acid, and the oil phase is water washed with appropriate means for selective extraction where required. The oil layer is sent on through a distillation train for recovery and purification of product acetone, recycle cumene, alpha methyl styrene (part or all of which may be hydrogenated and recycled), product phenol, and acetophenone, which may be purified for marketing or simply left with the residual oil for use as fuel, or for incineration.

III. Plant Emissions

A. Continuous Air Emissions

1. Feed Purification Vent

Literature references indicate the necessity for "clean" cumene feed and certainly those who find alpha methyl styrene unmarketable must hydrogenate this material for recycle. However, only respondent 22-1 mentions feed purification, and his information suggests that emissions here are negligible.

2. Oxidizer Vent

"Spent air" exhausted from the oxidizer is the largest single source of emissions from cumene process phenol plants. Although not all respondents provided details, it appears that multiple stage condensing systems involving refrigeration under moderate pressures up to 70 or 80 psig are virtually integral to the oxidation section. Variations in emissions are found because individual producers operate at a different pressure, cool to a different temperature, use a scrubber, rely on an activated carbon adsorber, or send the vent stream to an incinerator. Reported emissions, running from "trace" through .0015 up to .0067 tons/ton phenol normally (with occasional 1 to 4 hour equipment failure breaks, in one case up to .049 tons/ton phenol), are summarized in Table III.

3. Concentrator Vent

Where respondents reported emission for a post oxidizer cumene hydroperoxide concentrator vent (22-1, 22-6 and 22-6), emission levels were low, in the range .0003 tons/ton of phenol and less. Reported emissions summarized in Table III.

4. Cleavage Section Vent

Respondent information on cleavage section vent emissions is very meagre, with only one actual figure of .0002 tons/ton phenol reported. However, the fact that acetone is produced here, together with one respondent's design calculation figure of .0024 tons of acetone plus .0013 tons of aldehydes per ton of phenol indicates that low to moderate light hydrocarbon emissions from cleavage may be "normal". Reported emissions are summarized in Table III.

5. Distillation Train Vents

Acetone is the prominent emission component from this section of the plant, with some formaldehyde. Respondent 22-6 has calculated on the basis of vapor pressure over the analysed condensed liquid, and finds emissions at .0043 tons of acetone and .0003 tons of formaldehyde per ton of phenol from an acetone topping tower, and 22-4 uses design calculations to show acetone .0012 and formaldehyde .0009 tons/ton of phenol similarly. No other emissions of any consequence are reported, though trace amounts of cumene, mesityl oxide, and phenol are mentioned. See Table III for details.

6. Plant Flares and Boiler Operations

In some cases, waste "light oil", "heavy oil", or "heavy ends"

are sold or transferred to refinery sections of the overall plant for use as fuel. Respondent 22-3 reports continuous delivery of light and heavy oil waste to boilers for fuel, where excess air is reported to result (design basis) in complete combustion so that no significant air pollution occurs. Respondent 22-8 accumulates phenolic heavy ends and about once a month sends this liquid to a fuel gas fired flare, again with reported (design basis) complete combustion.

B. Intermittent Air Emissions

Aside from the intermittent flaring of liquid waste (see 6 above) the only intermittent air emissions involved are those associated with atmosphere venting during start-ups and plant emergencies, or in those cases where equipment changeover or refill is required, as with spent activated carbon sorbent. An example of the latter is mentioned by respondent 22-6 with regard to the infrequent direct venting of the oxidizer off-gas (averaging $\sim .04$ and up to .049 tons of hydrocarbon emission/ton of phenol) when spent activated carbon sorber is taken off the line. Another example is given by respondent 22-8, again with regard to venting of the oxidizer off-gas (hydrocarbon emissions up to as high as .004 tons/ton of phenol for 1 to 4 hour periods possibly ten times per year when "recovery equipment (may) fail"). Emissions in this category may be expected to vary greatly, and no valid "normal" figure can be inferred from the information at hand.

C. Continuous Liquid Wastes

1. Heavy Ends

"Phenolic heavy ends" or "light" and "a heavy oil" or "residual fuel" bottoms from the distillation train most certainly have to be disposed of one way or another. Literature information indicates that the amount of heavy oil waste is roughly 0.1000 tons per ton of phenol product. The six respondents providing information on this point gave figures running from .05 to .26, with a comparable average of 0.11 tons per ton of phenol, though accompanying charge stock or product components considered not worth recovering would raise the actual amount of "waste" perhaps 50%, or even more, in some cases.

Only three respondents actually indicated how their residual oil was handled, and in each case incineration or flaring with fuel gas was reported. Complete combustion, with no significant air pollution emissions is the design basis, although some NO_x probably forms.

2. Aqueous Waste

Acidic waste wash water from the cleavage reactor separator has been combined together with aqueous phenolic waste streams and other waste water in figures supplied by the respondents, though presumably some selective handling is practiced in disposal. The total amounts handled and method of disposal was reported as follows:

<u>Respondent Code</u>	<u>Tons waste water per ton phenol</u>	<u>Disposal Method</u>
22-1	15.9	Refinery treating system

<u>Respondent Code</u>	<u>Tons waste water per ton phenol</u>	<u>Disposal Method</u>
22-3	1.6	Injection well
22-4	2.2	-
22-5	?	Injection well
22-6	1.6	In-plant waste treatment
22-7	4.3	-
22-8	0.33	In-plant waste treatment
22-9	0.13	Refinery waste treatment

D. Solid Wastes

Only respondents reporting solid wastes were 22-7, with an undefined 81,000 lb./month, 22-8, with 50,000 lb./year of diatomaceous earth for water filtration sent to in-plant land fill, and 22-9, with 100 lb. waste solid disposed of on company property.

E. Odors

There was no mention of odor complaints during the past year by any of the eight respondents. Six of the respondents reported in-plant odor problems associated with the oxidation section (mainly cumene), with no complaints mentioned, and only infrequent off-plant odors noted from this source by two of those reporting. Respondents 22-4 and 22-6 mentioned in-plant odor from the acetone topping unit, with the latter referring to infrequent off-plant odor being observed from this source, though again, no complaints. The 22-6 alpha methyl styrene tower had in-plant odor problems, again infrequently off-plant. Only respondent 22-8 mentioned odor from the cleavage section, and this was in-plant. Only respondent 22-1 mentioned phenolic type odors, and these were said to be associated with a phenolic water sump and a process bottoms transfer pump, detectable only on plant property. Respondent 22-8 reported that on occasions when the fuel gas fired incinerator was used to burn liquid phenol waste, there was an odor (not identified) on the plant property, and infrequently off-plant, though no complaints had been noted.

F. Fugitive Emissions

Most producers made no attempt to estimate fugitive emissions. Respondents who did make estimates provided figures which compare as shown here in the right hand column.

<u>Respondent Code No.</u>	<u>Identified Emissions total tons/ton phenol</u>	<u>Fugitive or "other emissions" total tons/ton phenol</u>
22-1	.0028	.0005
22-4	.0091	.0003
22-6	.0046	.0010

In some cases, mention was made of fugitive emissions involving leaks from pump seals, valve stems, packing glands, waste oil end water sumps, etc., with no attempt at an estimate. One respondent lumped all emissions and leakage together without distinguishing air

or water pollutants, by suggesting approximately 2% losses according to weight balance on cumene charge, a figure equivalent to .0285 tons per ton of phenol. This figure is high, but perhaps has meaning in terms of potential for air and water pollution together.

Calculations based on vapor pressure and tank volume and turnovers per year provide an upper limit estimate for losses to atmosphere from storage tanks. The total hydrocarbon figures obtained in this way vary greatly, from less than .00001 tons/ton of phenol to as much as .0018 tons/ton, in most cases the major portion being acetone. In many cases, producers have floating roof tanks or have installed N₂ blanket or other type conservation vents, or else the tanks are normally kept filled. The one respondent from California had apparently provided floating roof or vapor seal devices so that tankage vapor losses were virtually eliminated.

None of the respondents gave any figures for appreciable actual phenol emissions, and with its low vapor pressure, one would not expect much loss to the atmosphere. However, phenol is highly toxic, and does have an extremely low TLV or threshold limit value in air, set by the American Conference of Governmental Industrial Hygienists, as recorded by N. Irving Sax in "Dangerous Properties of Industrial Materials", 3rd Edition, (1968). Sax gives a recommended 5 ppm TLV for phenol, compared to a recommended 25 ppm for benzene or a tentative 50 ppm for cumene. Sax points out (page 3) that literal application of TL values is dangerous for a number of reasons.* Nevertheless, one can calculate that considerable quantities of air would be "contaminated" to the TLV level when, for example, a large phenol tank held at 130° F is filled with liquid phenol with vapor escaping through an unprotected vent to the atmosphere. For one respondent's tank conditions, assuming complete purging of the vapor space for each reported tank fill, the average daily phenol emission would be sufficient to bring a 400 x 400 foot square, 1000 foot depth layer of air to the 5 ppm TLV level. For another respondent, the volume of air brought to the 5 ppm phenol TLV level each day would correspond to 570 x 570 feet square and 1000 foot depth. Thus, on general principles, for a toxic material such as phenol, one might well recommend the installation of protected vent systems for storage tanks and other vessels wherever feasible.

*One of these being, of course, that material which is picked up by skin contact is included and thus makes establishment of air limits difficult.

IV. Emission Control

Table IV of this report, "Catalog of Emission Control Devices", provides a summary of the devices reported by operators of cumene process phenol plants. The control devices may be divided into two broad categories: (1) Combustion Devices - those which depend on thermal or catalytic oxidation of combustibles for emission control, and (2) Non-Combustion Devices - Those that do not depend on combustion. In Table IV, all combustion devices will be assigned two efficiency ratings (when data are available):

(1) CCR - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of O}_2 \text{ that react with pollutants in feed to device}}{\text{lbs. of O}_2 \text{ that theoretically could react with these pollutants}} \times 100$$

(2) SERR - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\text{weighted pollutants in} - \text{weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Most non-combustion devices will be assigned a Specific Efficiency, SE, based on percent reduction of a specific compound with that compound defined. A few non-combustion devices will receive SERR ratings.

In some cases, respondents included helpful information on a venting device which, when carefully maintained, provided effective emission control, but they were quick to point out that the device was really an economically necessary integral part of the plant equipment, therefore, not legitimately an emission control cost item. In other cases, the large amount of hydrocarbon recovery attributable to the device made it obvious that it was an economic necessity, but the difficult-to-assess incremental cost of further reducing condensate temperature, or maintaining a slightly higher pressure in a knock-out drum, or more frequent change over to a freshly reactivated carbon sorbent tower, or the like, might well be considered part of the expense of emission control.

Undoubtedly due, at least in part, to the strict attention being paid to environmental considerations in California, the one cumene process phenol producer responding to the questionnaire from that state has installed devices on virtually every vent, outlet, or tank to keep air emissions low. It appears that emissions are indeed low for this plant, which is a small one, but unfortunately the respondent does not have quantitative data to provide a means for comparison with other plants.

The following is a brief summation of the various emission control devices identified by respondents in this survey. Details are to be found in Table IV with accompanying footnotes for that table.

Sorbers/Scrubbers

Activated carbon sorber beds are identified as effective emission control devices for recovering cumene from spent air from the oxidizer, by both 22-6 and 22-7 respondents; respondent 22-3 likewise mentions that activated carbon is used to advantage in the same location, but

ordinarily relies on a gas fired incinerator for further clean-up of this high volume effluent stream (see below).

Pressure and temperature conditions for the stream entering the PH-VII carbon bed are such that a relatively high cumene content is present, and the device, with a specific efficiency of 91%, is shown to recover sufficient cumene in one year's time to pay off the installed cost. Carbon sorber PH-VIII is also effective, though its Specific Efficiency is only 82% and the respondent had no operating cost figures.

"Scrubber" device PH-I listed by 22-1 is merely a water seal leg trap on the feed purification system, and water "scrubber" tank PH-XIV is a "catch-all" emergency relief provision which also serves to scrub normal wash section vents from several plant locations.

The "Scrubber-Cooler" device, which is part of the PH-II combination emission control used by 22-1 to recover cumene from the oxidizer off-gas, must really be considered an integral part of the plant, an economic necessity. It involves circulation of cooled cumene condensate down a 15 tray column to recover cumene in the vent stream and return to the oxidizer.

Condensers and V. O. Drums

Respondents 22-1, 22-4 and 22-5 all rely on refrigerated condensing equipment with knock-out drums under moderate pressure to achieve substantial removal of cumene from the oxidizer off-gas, with PH-II, PH-V and PH-VI respectively. In all three cases, the equipment is primarily needed for returning cumene to the oxidizer and only secondarily is an emission control device. Respondent 22-1 used a three stage water condenser, PH-III to control emission from the post oxidation concentrators, obtaining 65% Specific Efficiency, incurring a net cost in the operations. Respondent 22-4, with water condenser PH-IX above a post-oxidation wash unit, really considers this an economic necessity, hence, provided no recovery or operating cost data.

Respondent 22-1 shows single cold water condensers with knock-out drums PH-X and PH-XI for the cleavage reactor and an acetone tower, respectively; two-stage cold water condensers with steam jet ejectors and knock-out drums (PH-XII and PH-XIII) for acetone purification and phenol recovery, respectively. In each case the equipment is a legitimate emission control cost item, but there is insufficient data provided to allow an estimate of efficiency.

Incineration Devices

Producer 22-3 identifies a gas-fired incinerator PH-IV normally* serving to virtually eliminate hydrocarbon emissions from the oxidizer off-gas that has already passed through what appears to be fairly efficient activated carbon beds. Analytical data given indicate no unburned hydrocarbon or pollutant other than a trace of NO_x in the effluent, hence, virtually 100% Specific Efficiency.

Respondent 22-8 lists PH XV gas fired flare for periodic burning of heavy ends waste, and reports that on equipment design basis, combustion is complete, so 100% efficiency is indicated (though an infrequent off-plant

*Out of service for extensive repairs at the time of responding to the questionnaire, August, 1972.

odor problem is mentioned). Respondent 22-3 reports that both light and heavy oil waste is sent to plant boilers as fuel, but no information is provided to indicate efficiencies. Both of these incinerators probably cause the formation of at least traces of NO_x .

Future Possibilities

Among items mentioned by respondents for improvement in emission control were these:

1. Installation of vapor recovery or vapor conservation equipment on tanks.
2. Improvement in pump seals for phenolic stocks.
3. General process improvements. Areas for investigation in this regard include the following:
 - (a) Reexamination of proposals to use oxygen in place of air, with due emphasis on safety and economic considerations.
 - (b) Further use of refrigerated condenser equipment.
 - (c) Further use of hydrocarbon recovery systems like activated carbon.

V. Significance of Pollution

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate total weighted annual emissions of pollutants from these new plants. The results are summarized in Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index of 1,704 has been calculated in Table VII. This is well below the SEI's anticipated for other processes in the study.

Because of the relatively low SEI, it is recommended that no in-depth study of the Cumene Oxidation Process for the production of Phenol be undertaken in the current study. Although, a review of this recommendation may be justified at a future date. The reasons for review are somewhat subjective in nature, and no one of them would be justification on its own for an in-depth study. However, taken together they might be sufficiently important to warrant the collection of data that are pertinent to the setting of emission standards on new stationary sources. Briefly, these reasons are:

- 1) The reported oxidizer emissions factors range from a trace to nearly 0.01 with an emergency factor of nearly .05 reported in one instance. This is understandable since pollution control devices range from simple condenser systems through scrubbers to carbon absorbers and incinerators.
- 2) The reported oxidizer emissions include pollutants such as formaldehyde, acetophenone and cumene. If traces of cumene hydroperoxide are also present in this stream, it could be acid cleaved in the surroundings to form phenol.
- 3) Cleavage vents also contain noxious substances such as aldehydes.
- 4) Emission factors alone do not tell the story since some plants report emissions in terms of hundreds of pounds per hour of hydrocarbons or aldehydes.
- 5) An amount of liquid waste which is equivalent to about 10% of the production capacity is typically incinerated, which if uncontrolled could produce significant air pollution, especially NO_x or products of incomplete combustion.
- 6) Occasional off-plant odors are reported.
- 7) Phenol is highly toxic.
- 8) The process is clearly a growth one. Thus, economics of scale and new design might force shut downs of more marginal plants than were assumed in the prediction of the numbers of new plants. Hence, a greater number of candidates for new source standards would exist.
- 9) Phenol storage techniques are such that significant quantities of the substance could be emitted.

VI. Phenol Producers (vi, vii, viii)

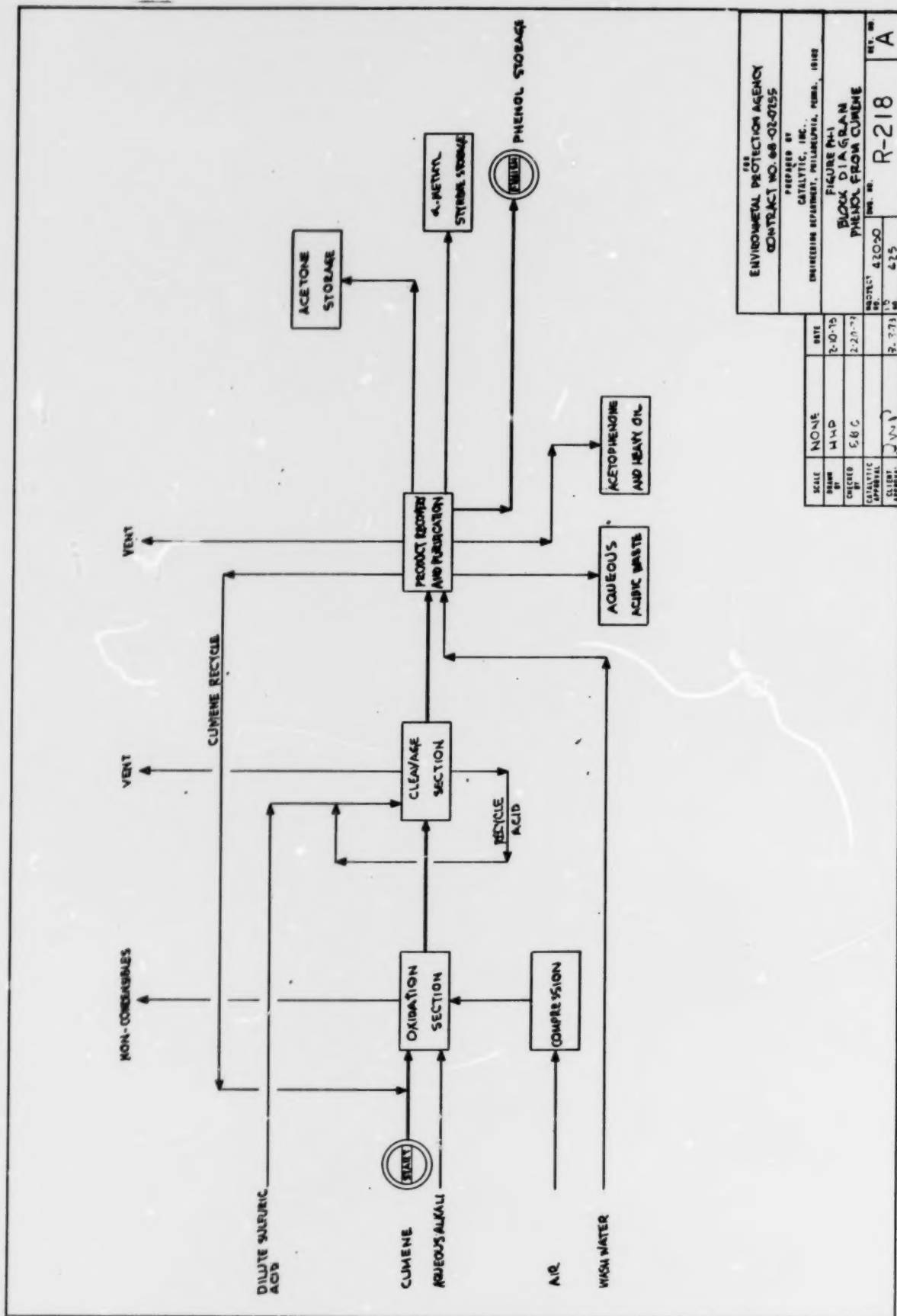
Natural phenol hardware capacity was about 60 MM pounds of phenol per year in 1972, but actual capacity was somewhat lower because of a scarcity of feedstocks for coal-tar derived material. Producers in this natural product category include Kaiser Steel, Fontana, California, Koppers Co., Inc., Follansbee, W. Va., Merichem Co., Houston, Texas, Productol Chemical, Santa Fe Springs, California, Stinson Lumber Co., Anascortes, Washington and U. S. Steel Corporation, Clairton, Pa.

Synthetic phenol, as mentioned previously, is derived from cumene for the most part, other processes being found unable to compete except for certain special circumstances. For example, as noted by Stanford Research Institute in "Chemical Economics Handbook", Dow Chemical maintains a benzene chlorination plant, Kalama Chemical, Inc. a toluene oxidation plant and Reichhold Chemicals, Inc. a benzene sulfonation plant because of special by-products obtained. Following is a list of companies and locations where synthetic phenol is now being produced (see CEH, July, 1972). In many cases, a large proportion of the capacity is committed for captive use.

Published Synthetic Phenol Capacity (1).

<u>Company</u>	<u>Location</u>	<u>Manufacturing Process</u>	<u>1972 Capacity MM Lb./Yr.</u>
Allied Chemical Corp.	Frankford, Pa.	Cumene	500
Clark Oil & Refining Corp.	Blue Island, Ill.	Cumene	75
Dow Chemical Co.	Oyster Creek, Texas	Cumene	400
	Midland, Mich.	Chlorina. Benzene	100
Georgia-Pacific Corp.	Palquemine, La.	Cumene	200
Kalama Chemical, Inc.	Kalama, Wash.	Toluene	48
Monsanto Co.	Chocolate Bayou, Texas	Cumene	375
Reichhold Chemicals	Tuscaloosa, Ala.	Sulfonation	135
Shell Chemical Co.	Houston, Texas	Cumene	60
Skelly Oil Co.	El Dorado, Kansas	Cumene	50
Std. Oil Co. of California	Richmond, Cal.	Cumene	55
Union Carbide Corp.	Bound Brook, N. J.	Cumene	150
	Penuelas, P. R.	Cumene	(2)
United States Steel Corp.	Haverhill, Ohio	Cumene	215 (3)
Total			2,363

- (1) As given by J. L. Blackford, July, 1972, Chemical Economics Handbook, Stanford Research Institute.
- (2) Union Carbide Penuelas, Puerto Rico, 200 MM Lb./Yr. new capacity, scheduled by January, 1973.
- (3) U. S. Steel, Haverhill plant capacity expansion up to 305 MM Lbs./Yr. in progress. see CW 1/31/73, page 19.



ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0155

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19106

FIGURE R-1
BLOCK DIAGRAM
PHENOL FROM CUMENE

PROJECT NO. 420-00
REV. NO. 425
REV. NO. R-218
A

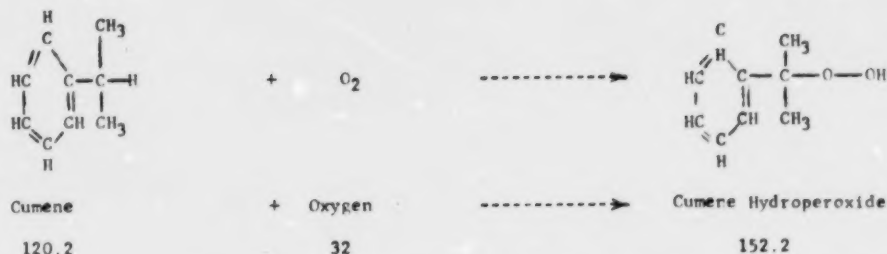
SCALE	DATE	NON-VENT
BASE	2-10-75	WHD
CHECKED BY	2-20-75	SCC
CATALYTIC APPROVAL		
CLIENT APPROVAL		

117

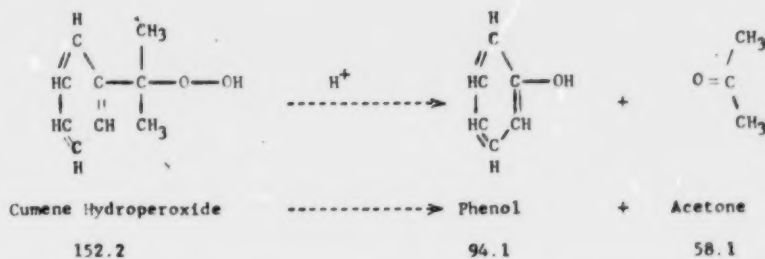
TABLE PH-I
BASIC CHEMISTRY
OF
PHENOL PRODUCTION FROM CUMENE (ix, x, xi, xii)

MAIN REACTION

I. Step A. Oxidation

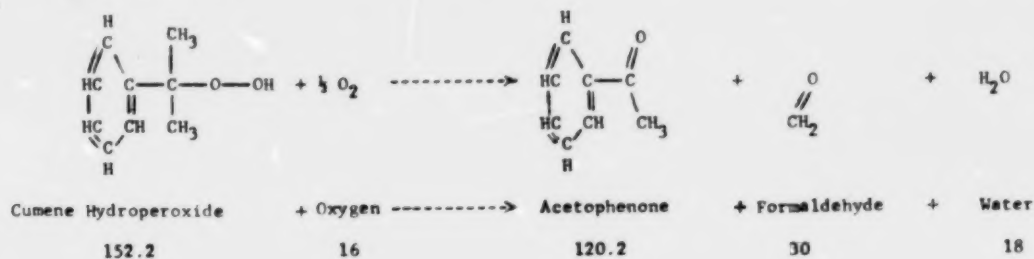


I. Step B. Cleavage



SECONDARY REACTIONS

II. Production of Acetophenone



III. Production of αMethylstyrene

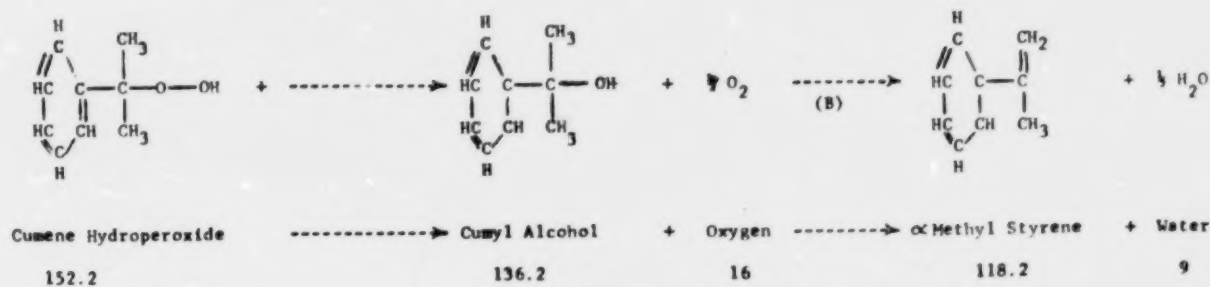


TABLE PH-II
PHENOL PRODUCTION EX CUMENE

MATERIAL BALANCE* TONS/TON OF PRODUCT

Stream No. (Fig. II)	(1)	(2)	(3)	(1, 2 & 3)	(5)	(6)	(7)	(8)
Stream Name	Oxidizing Air	Feed	Recycle	Gross Oxidizer Feed	Oxidizer Effluent	Vent	Cleavage Effluent	Acetone Tot. Ouid.
Cumene		1.4450	3.2611	4.7061	3.2611	.0029	3.2611	
Cumene Hydroperoxide					1.7621		1.0091	
Phenol							.6230	
Acetone							.1009	
<i>o</i> -Me-Styrene					.0505		.0505	
Acetophenone								
Formaldehyde	.5007			.5007		.0126		
Oxygen	1.7319			1.7319		.1100	.0137	
Nitrogen					.0052	1.7319		
Water						.0024	.0206	
Total	2.2326	1.4450	3.2611	6.9387	5.0789	1.8598	5.0789	.6204

119

Stream No. (Fig. II)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Stream Name	Acetone Tower Vent	Cumene Tower Op. L.	<i>o</i> -Me Styrene Tower Ouid.	Phenol Tower Btas.	Phenol Product	Alkali To Oxidizer	Make-up Acid	Wash Water	Wash Tower Btm.
Cumene		3.2611							
Cumene Hydroperoxide									
Phenol				.0091	1.0000				
Acetone	.0026								
<i>o</i> -Me-Styrene			.1009	.0505					
Acetophenone									
Formaldehyde									
Oxygen									
Nitrogen									
Water									
Total	.0026	3.2611	.1009	.0596	1.000				

Notes: "A" Oxidation is facilitated thru the use of an alkaline - aqueous emulsion - PH of 8.5 - 10.0 - a Na_2CO_3 solution is normally used with emulsifying agents, $\text{H}_2\text{O}/\text{oil}$ ratio is thought to be in the range of 2/1 to 5/1 (vol.).

"B" Dilute (~10%) sulfuric acid is recycled for cleavage - make-up rate is unknown.

"C" Wash water to remove residual acid, rate unspecified.

"D" Consists of wash water and residual H_2SO_4 .

*See notes "A" & "B" and Phenol Table II Material Balance Limitations.

Not Defined - See Note "D"

Not Defined - See Note "C"

Not Defined - See Note "B"

Not Defined - See Note "A"

PHENOL TABLE II MATERIAL BALANCE LIMITATIONS

1. Cumene conversion is set @ 30.7%; conversion usually reported between 25 and 45%.
2. Selectivity (moles phenol formed/moles cumene converted expressed as %) is set @ 88.4%. If methyl styrene is hydrogenated and recycled so that $\frac{1}{2}$ goes to phenol, selectivity would be 92%. Since demand for XMS is less than $\frac{1}{2}$ rated capacity, recycle is often preferred.
3. A review of respondents data reveals that heavy residual material amounting to ~.1000 tons/ton of phenol is produced. This is not included in the material balance shown here because definitive composition information is lacking. If it be assumed that a like amount of cumene (0.1000 tons/ton of phenol) be consumed producing this heavy material, along with recycle of methyl styrene (see 2 above) a selectivity of 86 mole % would be realized, in line with the average figure reported by the eight respondents in the present study.
4. Oxidizing air fixed at 50 lb./100 lb. product phenol, which is ~140% of theoretical for conversion and selectivity shown.
5. Hydrocarbons are shown only for the two vent streams (6) and (9) where emissions are appreciable, though other vent streams do contain measurable emissions, as indicated in Table III.
6. All cumene recycle here is shown in cleavage section effluent, though, as indicated in Figure II, some proportion is usually taken out for recycle following oxidation and/or concentration.
7. Water amounts shown here represent only reaction product as indicated in Table I where formaldehyde and methyl styrene are produced. Substantial quantities of water are required for the alkaline aqueous emulsion in the oxidation section (2 to 5 times hydrocarbons present), for the dilute sulfuric acid (~10% concentration) in the cleavage section, and in the subsequent wash tower.

TABLE PH-IIA
PRODUCTION OF PHENOL FROM CUMENE
GROSS HEAT BALANCE (xiii, xiv, xv)

BASIS MATERIAL BALANCE TABLE II
AND REACTIONS IN TABLE I

<u>OXIDATION REACTOR</u>	<u>BTU/Lb. Phenol Product</u>	
	<u>Exothermic</u> (Cooling Req'd.)	<u>Endothermic</u> (Heating Req'd.)
Reaction I (A) producing cumene hydroperoxide	483	
" II " acetophenone	58	
Heating cumene charge from 90 to 250° F		346
Heating N ₂ & O ₂ from 90 to 250° F		<u>87</u>
Totals	541	433
Net heat exchange requirement (difference)	108	
<u>CLEAVAGE REACTOR</u>		
Reaction I (B) producing phenol & acetone	991	
Reactions III (A) producing cumyl alcohol and III (B) producing methyl styrene	31	
Cooling cumene from 250° F to 140° F	165	
Cooling cumene hydroperoxide & acetophenone to 140° F	<u>120</u>	
Totals	1,307	0
Net heat exchange requirement (difference)	1,307	

122

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Page 2 of 13

Plant - EPA Code Number
Capacity - Tons of Phenol/Yr.
Average Production - Tons of Phenol/Yr.
Quarterly Production Variation - % of Max.
Emissions to Atmosphere
Stream

22-1
26,500
26,500
0

Flow - Lb./Hr.
Flow Characteristics - Continuous or Intermittent
if Intermittent - Hrs./Yr. flow
Composition - Tons/Ton of Phenol (5)

Phenol & Acetone
Sep'n./Purification
Section
Vapor Cond. Vents
Unknown
Continuous
Phenol Recovery &
Sep'n. Section
Vapor Cond.
Vent
Unknown
Continuous
Residual
Oil
Sump
Vent
Unknown
Continuous
Phenolic
Water
Sump
Vent
Unknown
Continuous

(+)

(+)

+

(+)

(+)

(+)

No port
Never
Yes (8)

No port
Never
No (6)

Elevated
Never
No

Elevated (7)
Never
No

1
24
6
Ambient
None

1
30
2
Ambient
Yes

1
125
3
Ambient
Yes

1
120
3
Ambient
Yes

Yes
(6)
PH-XIV
(+)
0

Vapor Condenser
PH-XIII
(+)
0

Vapor Condenser
PH-XI, XII
(+)
0

Catalog I. D. Number
Total Hydrocarbon Emission - Ton/Ton of Phenol
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol
Total NO_x Emissions - Ton/Ton of Phenol
Total SO_x Emissions - Ton/Ton of Phenol
Total CO Emissions - Ton/Ton of Phenol

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Page 3 of 13

Plant - EPA Code Number	22-1	Misc Vent	Process Bottoms
Capacity - Tons of Phenol/Yr.	26,500	Water Scrubber	Transfer
Average Production - Tons of Phenol/Yr.	26,500	Stack #10	Pump
Quarterly Production Variation - % of Max.	0	Unknown	Unknown
Emissions to Atmosphere		Continuous	(occasional)
Stream			
Flow - Lb./Hr.			
Flow Characteristics - Continuous or Intermittent			
if Intermittent - Hrs./Yr. Flow			
Composition - Tons/Ton of Phenol (5)			
Cumene			
Cumene Hydroperoxide			
Phenol			
Acetone			
Methyl Styrene			
Acetophenone			
Acetaldehyde			
Formaldehyde			
Mesityl Oxide			
Dimethyl Benzyl Alcohol			
Benzene			
Toluene			
Ethyl Benzene			
Misc. Hydrocarbons			
Cumyl Phenol & Phenolic Tars			
Water			
Carbon Dioxide			
Nitrogen			
Oxygen			
Sample Tap Location			
Date or Frequency of Sampling			
Type of Analysis			
Odor Problems			
Vent Stacks			
Flow - SCFM/stack			
Number			
Height - Feet			
Diameter - Inches			
Exit Gas Temp. °F			
Emission Control Devices			
Type - Incinerator			
Flare			
Scrubber			
Other			
Catalog I. D. Number			
Total Hydrocarbon Emissions - Ton/Ton of Phenol			
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol			
Total NO _x Emissions - Ton/Ton of Phenol			
Total SO _x Emissions - Ton/Ton of Phenol			
Total CO Emissions - Ton/Ton of Phenol			
Need platform (7)			
Never			
No			
At grade (7)			
Once (1972)			
G.C. ±5%			
No			
.29			
1			
70			
2			
Ambient			
None			
Yes			
PH-XIV (11)			
(+)			
0			
(+)			
0			

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Page 4 of 13

Plant - EPA Code Number
Capacity - Tons of Phenol/Yr.
Average Production - Tons of Phenol/Yr.
Quarterly Production Variation - % of Avg.
Stream

Flow - Lb./Hr.
Flow Characteristics - Continuous or Intermittent
If Intermittent - Hrs./Yr. Flow
Composition - Tons/Ton of Phenol (5)

Cumene
Cumene Hydroperoxide
Phenol
Acetone
Methyl Styrene
Acetophenone
Acetaldehyde
Formaldehyde
Mesityl Oxide
Dimethyl Benzyl Alcohol
Benzene
Toluene
Ethyl Benzene
Misc. Hydrocarbons
Cumyl Phenol & Phenolic Tars
Water
Carbon Dioxide
Nitrogen
Oxygen

Sample Tap Location
Date or Frequency of Sampling
Type of Analysis
Odor Problem

Vent Stacks
Flow - SCFH/stack
Number

Height - Feet
Diameter - Inches
Exit Gas Temp. °F

Emission Control Devices
Type - Incinerator
Flare
Scrubber
Other

Catalog I. D. Number

Total Hydrocarbon Emissions - Ton/Ton of Phenol
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol
Total NO_x Emissions - Ton/Ton of Phenol
Total SO_x Emissions - Ton/Ton of Phenol
Total CO Emissions - Ton/Ton of Phenol

Oxidation Section Vent 114,300 (13) Continuous 0 to .005
Oxidation Incinerator Stack 128,600 (13), (15) Continuous
Casee (Calc.) ex Incineration of Heavy Oil Waste 142,000 (17) Continuous

0 to .005

(+)

"trace" (orgs.)

0 to .0024

2.2625

.1190

Stairway access at original start-up Org. G.C. +20% Yes (in plant) (14)

25,700

50°

Active. Carbon (12)

0 to .005 (12)

(+)

Trace

+

+

Difficult

Never

No (15)

20,250

1

55

72

450°

Yes (15)

Boiler (Fuel)

Boiler #1

PH-IV

(+)

"trace"

0

Boiler (Fuel)

Boiler #2

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Page 5 of 13

Plant - EPA Code Number	22-4 (21)	Acetone Topping Column Overhead Accumulator
Capacity - Tons of Phenol/Yr.	125,000	
Average Production - Tons of Phenol/Yr.	125,000	
Quarterly Production Variation - % of Max. Stream	0	
Flow - lb./hr.		
Flow Characteristics - Continuous or Intermittent		
If Intermittent - Hrs./Yr. Flow		
Composition - Tons/Ton of Phenol (5)		
Cumene		
Cumene Hydroperoxide		
Phenol		
Acetone		
Methyl Styrene		
Acetophenone		
Acetaldehyde		
Formaldehyde		
Methyl Oxide		
Dimethyl Benzyl Alcohol		
Benzene		
Toluene		
Ethyl Benzene		
Misc. Hydrocarbons		
Cumyl Phenol & Phenolic Tars		
Water		
Carbon Dioxide		
Nitrogen		
Oxygen		
Sample Tap Location		
Date or Frequency of Sampling		
Type of Analysis		
Odor Problem		
Vent Stacks		
Flow - SCFH/stack		
Number		
Height - Feet		
Diameter - Inches		
Exit Gas Temp. Of		
Emission Control Devices		
Type - Incinerator		
Flare		
Scrubber		
Other		
Catalog I. D. Number		
Total Hydrocarbon Emissions - Ton/Ton of Phenol		
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol		
Total NO _x Emissions - Ton/Ton of Phenol		
Total SO _x Emissions - Ton/Ton of Phenol		
Total CO Emissions - Ton/Ton of Phenol		
Oxidizer Section Vent	53,500 (19) Continuous	Post Oxidizer Washer, Surge Tank Combination Vent 790 (19) Continuous
Cumene Stripper Jet Condenser Vent	Unknown Continuous	Acetone Topping Column Overhead Accumulator
Refrigerator PH-V	73 psig Cond. (20) PH-V 0067	Refrigerator PH-IX 0003
Refrigerator PH-IX	18 psig Chiller (20) PH-IX 0003	C. W. Condenser C. W. Condenser 0021

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Page 6 of 13

Plant - EPA Code Number
Capacity - Tons of Phenol/Yr.
Average Production - Tons of Phenol/Yr.
Quarterly Production Variation - % Of Max.
Stream

22-4 (21)
125,000
125,000

Post Cleavage Reactor Vapor Condenser Vent	Post Cleavage Washer Vent	Phenol-Acetone Still Vapor Condenser Vent	Acetone Column Vapor Condenser Vent	Phenol Recovery Overhead Accumulator Section Vent
Unknown Continuous	Unknown Continuous	Unknown Continuous	Unknown Continuous	Unknown Continuous

Flow - Lb./Hr.
Flow Characteristics - Continuous or Intermittent
if Intermittent - Hrs./Yr. Flow
Composition - Tons/Ton of Phenol (5)

Cumene Hydroperoxide
Phenol

Acetone:

Methyl Styrene

Acetophenone

Acetaldehyde

Formaldehyde

Mesityl Oxide

Dimethyl Benzyl Alcohol

Benzene

Toluene

Ethyl Benzene

Misc. Hydrocarbons

Cumyl Phenol & Phenolic Tars

Water

Carbon Dioxide

Nitrogen

Sample Tap Location
Date or Frequency of Sampling

Type of Analysis

Odor Problem

Vent Stacks

Flow - SCFM/stack

Number

Height - Feet

Diameter - Inches

Exit Gas Temp. Of

Emission Control Devices

Type - Incinerator

Flare

Scrubber

Other

C. W. Condenser

C. W. Condenser

Condenser

Catalog I. D. Number
Total Hydrocarbon Emissions - Ton/Ton of Phenol
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol
Total NO_x Emissions - Ton/Ton of Phenol
Total SO_x Emissions - Ton/Ton of Phenol
Total CO Emissions - Ton/Ton of Phenol

100

1

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Plant - EPA Code Number	22-6	100,000	100,000	0																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
-------------------------	------	---------	---------	---	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Plant - EPA Code Number	Capacity - Tons of Phenol/Yr.	Average Production - Tons of Phenol/Yr.	Quarterly Production Variation - % of Max.	Emissions to Atmosphere	Stream
22-7	40,000	40,000	0		
	Post Oxidizer Carbon Sorber Vent	23,800 (28) Continuous	No data Continuous	Phenol Recovery Purification Vent	Product Recovery Section Steam Jet Vent
	Acetone				Acetone Recovery Section Vent
	Flow Characteristics - Continuous or Intermittent If Intermittent - Hrs./Yr. Flow Composition - Tons/Ton of Phenol (5)				
	Cumene	.0029			
	Cumene Hydroperoxide				
	Phenol				
	Acetone				
	Methyl Styrene				
	Acetophenone				
	Acetaldehyde				
	Formaldehyde				
	Hexyl Oxide				
	Dimethyl Benzyl Alcohol				
	Benzene				
	Toluene				
	Ethyl Benzene				
	Misc. Hydrocarbons				
	Cumyl Phenol & Phenolic Tars				
	Water				
	Carbon Dioxide				
	Nitrogen				
	Oxygen				
	Sample Tap Location				
	Date or Frequency of Sampling				
	Type of Analysis				
	Odor Problems				
	Vent Stacks				
	Flow - SCFM/stack				
	Number				
	Height - Feet				
	Diameter - Inches				
	Exit Gas Temp. Of				
	Emission Control Devices				
	Type - Incinerator				
	Flare				
	Scrubber				
	Other				
	Catalog I. D. Number				
	Total Hydrocarbon Emissions - Ton/Ton of Phenol				
	Total Particulate & Aerosol Emissions - Ton/Ton of Phenol				
	Total NO _x Emissions - Ton/Ton of Phenol				
	Total SO _x Emissions - Ton/Ton of Phenol				
	Total CO Emissions - Ton/Ton of Phenol				

Page 11 of 13

132

Plant - EPA Code Number
Capacity - Tons of Phenol
Average Production - Tons
Quarterly Production Variations
Emissions to Atmosphere
Stream

Flow - Lb./Hr.
Flow Characteristics - Continuous or
if Intermittent - Hrs./Yr. Flow
Composition - Tons/Yr. of Material (5)

Stream	Post Oxidizer	CHP Conc'n. & Decomp. Section	Raw Acetone Column	Cumene Column	Methyl Styrene Column
	Recovery Section	Steam Educator	Vent	Steam Educator	Steam Educator
Flow - Lb./Hr.	11,270 (32)	Unknown	Unknown	Unknown	Unknown
Flow Characteristics - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow					
Composition - Tons/Yen of Phenol (5)					
Cumene	+			(+)	(+)
Cumene Hydroperoxide					
Phenol					
Acetone			+		
Methyl Styrene					
Acetophenone			(+)		
Acetaldehyde			(+)		
Formaldehyde					
Mesityl Oxide		(+)			(+)
Dimethyl Benzyl Alcohol					
Benzene					
Toluene					
Ethyl Benzene					
Misc. Hydrocarbons					
Cumyl Phenol & Phenolic Tars					
Water	+	+		+	+
Nitrogen					
Oxygen					
Sample Tap Location	1.6744		(+)		
Date or Frequency of Sampling	None, difficult				
Type of Analysis	Never	Very difficult	Never	Very difficult	Very difficult
Odor Problems	None	None	None	None	None
Odor Problems	Yes, off plant infreq.	None	"Not applicable"	None	None
Vent Stacks					
Flow - SCFM/stack	2500				
Number	1	2	1	1	1
Height - Feet	45	57	80	105	95
Diameter - Inches	14	1.5	3	1.5	1.5
Exit Gas Temp. °F	700	2000	700	2000	2000
Emission Control Devices					
Type - Incinerator					
Flare					
Scrubber					
Other					

Catalog I. D. Number

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Plant - EPA Code Number	Capacity - Tons of Phenol/Yr.	Average Production - Tons of Phenol/Yr.	Quarterly Production Variation - % of Max.	Emissions to Atmosphere	Phenol Column Steam Eductor Vent Unknown Continuous	Residue Stripper Steam Eductor Vent Unknown Continuous	Acetone Dilution Column Vent Unknown Continuous	Acetone Concentration Column Vent Unknown Continuous	Acetophenone Purification Hatch Still Steam Eductor Unknown Intermittent
	22-9	28,500	28,500	29					
Flow - Lb./Hr.									
Flow Characteristics - Continuous or Intermittent									
If Intermittent - Hrs./Yr. Flow									
Composition - Tons/Ton of Phenol (%)									
Cumene									
Cumene Hydroperoxide									
Phenol									
Acetone									
Methyl Styrene									
Acetophenone									
Acetaldehyde									
Formaldehyde									
Mesityl Oxide									
Dimethyl Benzyl Alcohol									
Benzene									
Toluene									
Ethyl Benzene									
Misc. Hydrocarbons									
Cumyl Phenol & Phenolic Tars									
Water									
Carbon Dioxide									
Nitrogen									
Oxygen									
Sample Tap Location									
Date or Frequency of Sampling									
Type of Analysis									
Odor Problems									
Vent Stacks									
Flow - SCFM/stack									
Number									
Height - Feet									
Diameter - Inches									
Exit Gas Temp. of									
Emission Control Devices									
Type - Incinerator									
Flare									
Scrubber									
Other									
Catalog I. D. Number									
Total Hydrocarbon Emissions - Ton/Ton of Phenol									
Total Particulate & Aerosol Emissions - Ton/Ton of Phenol									
Total NO _x Emissions - Ton/Ton of Phenol									
Total SO _x Emissions - Ton/Ton of Phenol									
Total CO Emissions - Ton/Ton of Phenol									

EXPLANATION OF NOTES
TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

- (1) No information given for estimating emissions. device presumably releases some small quantities of hydrocarbons.
- (2) Since sampling involved plant operation @ 85% of capacity, stream flow has been adjusted in simple proportion to correspond to 100% capacity rate.
- (3) Toluene, ethyl benzene and cumene here accounted for as cumene.
- (4) Vents from PH-XI and PH-XII are combined and presumably carry acetone vapor, but the amount is unknown, and no odor problem is indicated.
- (5) The (+) notations shown here were not reported by the particular respondent, but indicate probable presence of at least a trace emission as judged from specific process step, in line with other respondents information on a like stream.
- (6) Sump seal and vent improved in 1970 to eliminate a previous occasional in-plant odor emission.
- (7) Hazardous area, protective clothing and gear required.
- (8) Phenolic odor occasionally detectable on plant property.
- (9) Sampled during capacity operation.
- (10) Vents from acetone purification, post-cleavage neutralizing and wash section and phenolic water stripper, together with occasional emergency relief, delivered to scrubber PH-XIV.
- (11) Total for other emissions, including occasional pump seal and other minor leakages estimated by respondent at 30,000 lbs. total hydrocarbons per year, equivalent to 0.0006 tons/ton phenol.
- (12) Freshly regenerated active carbon beds (not specifically identified by respondent) prevent organics in effluent to incinerator: spent carbon permits up to 0.2% organics in gas and stream to incinerator.
- (13) Sampled at ~70% production rate; stream flow proportionately adjusted to level corresponding to normal production rate of 48,000 lbs. phenol/hr.; stream for incinerator stack similarly adjusted.
- (14) Odor off property only one time when equipment malfunctioned.
- (15) Incinerator damaged by fire, undergoing repairs, but not in operation as of August 4, 1972.
- (16) Light oil liquid waste stream of 2,500 lbs./hr. from cleavage and distillation section (tons/ton of phenol amounts: .0260 cumene, .0078 AMS, .0078 acetone and .0104 other oils) pumped to boiler, and for present purpose assumed to undergo complete combustion with 100% excess air.

EXPLANATION OF NOTES
TABLE PH-III CONTINUED

- (17) Heavy oil liquid waste stream of 6,000 lb./hour from cleavage and distillation section (tons/ton of phenol amounts: .00625 cumene, .0375 phenol, .01875 acetophenone and .0625 liquid "heavies") pumped to second boiler, and for present purpose assumed to undergo complete combustion with 100% excess air.
- (18) Liquid streams analysed before pumping to boilers.
- (19) Data calculated from engineering design using known vapor pressures of components, with exception of O₂ which is continuously metered and analysed.
- (20) System primarily designed for material recovery, hence, not listed as an air pollution control cost.
- (21) Vent streams believed to be carrying less than 10 lbs. of organic flow per hour were not surveyed in answer to the questionnaire; only two of these streams involved have measurable organic flow, and these together were estimated at 11 lbs./hour, equivalent to about 0.0003 tons/ton of phenol.
- (22) Figures given calculated from design material balances supplied by original contractor.
- (23) This vent stream, which can have as high as .049 tons organic emissions/ton of phenol, is sent to PH-VII activated charcoal adsorption recovery system, which normally is in service and removes about 90% of organics present.
- (24) Depending on time since last regeneration, PH-VII effluent can go to .0109 tons organic emissions/ton phenol.
- (25) Higher in warm weather, $\pm$ 40% over year.
- (26) Flow (rate unknown) has been observed ~6 times/month over 4 months, or 20% the time, while operating @ 100 - 110% of design capacity, the stream consists primarily of acetone.
- (27) Other emissions believed to be insignificant relative to thru-put (~0.17 or ~0.0010 tons/ton phenol).
- (28) Sampled at 93.8% of capacity, figures adjusted.
- (29) Hydrocarbons can reach 0.0240 tons/ton phenol ten times per year for 1 - 4 hours each time, when recovery system failure occurs.
- (30) Combined concentration section vents ~125° F exit gas temperature, cleavage section ~125° F, recovery section ~150° F.
- (31) Flare operated to burn an annual total of 500,000 lbs. phenolic heavy ends @ 3,000 lb./hour. 12 times per year for 14 hours each occurrence at (intermittent) flow rate shown. Design burner feed operation with 100% excess O₂ assumed together with steam injection ratio of 2 lb. steam per 1 lb. hydrocarbon fuel, assuming complete combustion.

EXPLANATION OF NOTES
TABLE PH-III CONTINUED

- (32) Design calculation.
- (33) Other emissions not known, total loss for unit may be approximately 2 wt. % of cumene charged as determined by material balance. (Equivalent to 0.0200 tons/ton phenol).

TABLE PH-IV
CATALOG OF EMISSION CONTROL DEVICES
PRODUCTION OF PHENOL FROM CUMENE

Page 1 of 3

Plant Section	Device Class	EPA Code No. for plant using	Flow Diagram (Fig. 11) Stream I. D.	Device I. D. No.	Purpose - Control Emission of	Feed Purification	Scrubber Condenser (2)	Oxidation	Incinerator (7)	Condenser (8)
SCRUBBING/SORBING MEDIUM						Scrubber	Scrubber Condenser (2)	Condenser (6)	Incinerator (7)	Condenser (8)
Type - Spray						22-1	22-1	22-1	22-3	22-4
Packed Column(s)						PH-I	PH-II	PH-III	PH-IV	PH-V
Trays - Type						Hydrocarbons	Hydrocarbons	Hydrocarbons	Hydrocarbons	Hydrocarbons
Number										
Plenum Chamber						Water (1)	Cumene			
Other										
Scrubbing/Sorbing Medium Usage - GPM (lbs./lb. phenol)						Seal Leg Trap				
Design Temp. (operating temp.) °F						~1000 GP Yr.				
Gas Rate - SCFM (lb./hr.)						Ambient	100 (3) 40 (3) 40	8 7	(80,000)	(73,300)
T-I Height - Ft.						Unknown	43			
Diameter - Ft.						?	3.5			
Wash/Vent Gases to stack						Yes	.167			Vent
Stack Height - Ft.						112	.84			70
Stack Diameter - Ft.						.167				1.17
										Yes
										Yes
K. O. TYPE - CONDENSER & K. O. DRUM										
Demister										
Degasser										
Other										
Design Pressure (operating pressure) PSIG										
Flow Rate of Treated Stream										
Liquid - lb./hr. (GPM)							Unknown (recy.)	1.4		
Gas - lb./hr. (SCFM)							~ (3700) ~	(8.7)		
SCFM/Stack							~ 3700 ~	Water (6)		
Primary Condenser Refrigeration Liquid							Pre-12			
Capacity of Refrigeration Unit - Tons							.75	130		
Temperature to Condenser - (Sorber) - °F							100	Ambient		
Temperature out of Condenser - (Sorber) - °F							40			
Compound Types Incinerated										
Combustion Device - Flame										
Incinerator										
Other										
Materials to Incinerator - SCFM (lb./hr.)										
Auxiliary Fuel Req'd. (Excl. pilot)										
Type										
Rate BTU/Hr.										
Installed Cost - Mat'l. & Labor \$							100,000	20,000	(80,000)	300,000
Installed Cost Based on "year" - dollars							1953	1953	Yes	1970
Installed Cost - Mat'l. & Labor - c/lb. of phenol/yr.							.1887	.0377	Net. Gas	1700
Operating Cost - Annual - \$ (1972, excl. depreciation)							15,800	7,500	.0188	(8)
Value of Recovered - \$/Yr.							3,000 (4)	1,000	.06,000	
Net Operating Cost - Annual - \$ (excl. depreciation)							12,800	6,500	0	
Net Operating Cost - c/lb. of phenol								.0123	~ 50,000 (7)	(8)
Efficiency - % SE							87 (5)	.65	100	
Efficiency - % SERR							Virtual 100	.65	100	
							Virtual 100			

TABLE PH-IV
CATALOG OF EMISSION CONTROL DEVICES
PRODUCTION OF PHENOL FROM CUMENE

Plant Section		Oxidation		Cleave Reaction	
Device Class	Condenser (8)	Carbon Sorber (9)	Carbon Sorber (9)	Condenser	Condenser
EPA Code No. for plant using	22-5	22-6	22-7	22-4	22-1
Flow Diagram (Fig. II) Stream I, D.	PH-VI	PH-VII	PH-VIII	PH-IX	PH-X
Device I, D. No.	PH-VI	PH-VII	PH-VIII	PH-IX	PH-X
Purpose - Control Emission of	Hydrocarbons	Hydrocarbons	Hydrocarbons	Hydrocarbons	Hydrocarbons
SCRUBBING/SORBING MEDIUM					
Type - Spray					
Packed Column (s)					
Trays - Type					
Number					
Plenum Chamber					
Other					
Scrubbing/Sorbing Medium Usage - GPM (lbs./lb. phenol)					
Design Temp. (operating temp.) °F					
Gas Rate - SCFM (lb./hr.)					
T-T Height - Ft.					
Wash/Vent Gases to stack					
Stack Height - Ft.					
Stack Diameter - Ft.					
K. O. TYPE - CONDENSER & K. O. DRUM					
Demister					
Degasser					
Other					
Design Pressure (operating pressure) PSIG					
Flow Rate of Treated Stream					
Liquid - lb./hr. (GPM)					
Gas - lb./hr. (SCFM)					
SCFM/Stack					
Primary Condenser Refrigeration Liquid					
Capacity of Refrigeration Unit - Tons					
Temperature to Condenser - (Sorber) - °F					
Temperature out of Condenser - (Sorber) - °F					
Compound Types Incinerated					
Combustion Device - Flame					
Incinerator					
Other					
Materials to Incinerator - SCFM (lb./hr.)					
Auxiliary Fuel Req'd (Excl. pilot)					
Type					
Rate BTU/Hr.					
Installed Cost - Mat'l. & Labor - \$					
Installed Cost Based on "Year" - dollars					
Installed Cost - Mat'l. & Labor - c/lb. of Phenol/Yr.					
Operating Cost - Annual - \$ (1972, excl. depreciation)					
Value of Recovered - \$/Yr.					
Net Operating Cost - Annual - \$ (excl. depreciation)					
Net Operating Cost - c/lb. of Phenol					
Efficiency - % SE					
Efficiency - % SERR					

TABLE PH-11
CATALOG OF EMISSION CONTROL DEVICES
PRODUCTION OF PHENOL FROM CUMENE

Page 3 of 3

Plant Section	Acetone Tower Condenser 22-1 A PH-XI Hydrocarbons	Acetone Purification Condenser 22-1 A PH-XII Hydrocarbons	Phenol Recovery Condenser 22-1 A PH-XIII Hydrocarbons	Last Emergency Relief Vent 22-1 E-CO PH-XIV Phenolics & HCs Water	Product Recovery Incinerator 22-6 A PH-XV Heavy Ends (17)
Device Class					
EPA Code No. for plant units					
Flow Diagram (Fig. 11) Stream I, D.					
Device I, D. No.					
Purpose - Control Emission of					
SCRUBBING/SORBING MEDIUM					
Type - Spray					
Packed Column(s)					
Trays - Type					
Number					
Plenum Chamber					
Other					
Scrubbing/Sorbing Medium (Solvent - GPM (lbs./lb. phenol))					
Design Temp. (Operating Temp.) °F					
Gas Rate - SCFM (lb./hr.)					
T-T Height - Ft.					
Diameter - Ft.					
Wash/Vent (Gases to stack)					
Stack Height - Ft.					
Stack Diameter - Ft.					
E. O. TYPE - CONDENSER & E. O. DRAIN					
Demister					
Design Pressure (Operating pressure) psig					
Flow Rate of Treated Stream					
Liquid - lb./hr. (GPM)					
Gas - lb./hr. (SCFM)					
SCFM/Stack					
Primary Condenser Refrigeration Liquid					
Capacity of Refrigeration Unit - Tons					
Temperature to Condenser - (Sorber) - °F					
Temperature out of Condenser - (Sorber) - °F					
Compound Types Incinerated					
Combustion Device - Flare					
Incinerator					
Other					
Materials to Incinerator - SCFM (lb./hr.)					
Auxiliary Fuel Req'd. (Excl. pilot)					
Type					
Rate BTU/Hr.					
Installed Cost - Mat'l. & Labor - \$					
Installed Cost Based on "Year" - dollars					
Installed Cost - Mat'l. & Labor - \$/lb. of Phenol/Yr.					
Operating Cost - Annual - \$ (1972, excl. depreciation)					
Value of Recovered - \$/Yr.					
Net Operating Cost - Annual - \$ (excl. depreciation)					
Net Operating Cost - c/lb. of Phenol					
Efficiency - % SE (T. CCR)					
Efficiency - % SERR					

EXPLANATION OF NOTES
TABLE PH-IV
CATALOG OF EMISSION CONTROL DEVICES
PRODUCTION OF PHENOL FROM CUMENE

- (1) Effluent water is sent to phenolic water stripper, which is vented through PH-XIV.
- (2) Device PH-II involves a combination of a water-cooled vent gas scrubber-cooler and a knock-out drum operating at 80 PSIG.
- (3) Outlet temperatures for scrubber-cooler and subsequent refrigerated condenser respectively (PH-II).
- (4) Vapor pressure calculation for temperatures indicated around this PH-II device show very good agreement with the amount of cumene reported leaving the oxidizer, but consistent vapor pressure calculations for cumene leaving the scrubber and then escaping the post refrigeration knock-out drum suggest a cumene recovered value (@ \$.032/lb.) for the latter (refrigerated condenser) of \$.39,000, it may be that recovery costs do not allow full credit.
- (5) Specific efficiency (SE) calculated using vapor pressure data around the refrigerated condenser and knock-out drum. SE for the entire scrubber-condenser unit is 99.4%, but at least the scrubber section must be considered an economically necessary integral part of the process equipment.
- (6) Three-stage water condenser with steam jet ejectors.
- (7) Incinerator PH-IV, normally operating @ 1400° F with 400° F exit gas, was out of service for repairs when the questionnaire was filled out in August, 1972, due to damage by fire. Operating costs for 1972 include \$20,000 maintenance, high due to repairs needed; net operating cost given here assumes \$10,000 maintenance for normal year. Respondent 22-3 reports that the oxidizer section effluent stream normally sent to PH-IV incinerator actually comes from activated carbon beds, which can allow as much as 0.2% organics (= up to .0033 tons cumene/ton phenol) emissions when activated carbon bed recovery equipment is near exhaustion.
- (8) Two-stage cooling system, with a water-cooled and a refrigerated condenser, each followed by 73 PSIG knock-out drums, with final release of uncondensable gas to atmosphere; this PH-VI unit is an economic necessity (respondent 22-4 reports recovery of 99% of the 20,000 lb./hour hydrocarbon content) and only secondarily an emission control device, hence, no assignable operating costs for emission control as such.
- (9) Two beds down-flow operation ($\Delta P \sim 28$ PSI for PH-VII 22-6) alternately, with upflow low-pressure steam regeneration, recondensation and recycle of recovered cumene.
- (10) Figure given is double the installed cost of a new adsorber installed by 22-7 in 1969; cost of original PH-VIII adsorbers unknown.
- (11) Negative numbers here indicate credit.
- (12) Credit shown does not take 22-7 PH-VIII operating costs (unknown) into account.

EXPLANATION OF NOTES
TABLE PH-IV CONTINUED

- (13) This PH-IX condenser, according to 22-4 respondent, is primarily designed for material recovery, thus considered inappropriate as an air pollution control cost.
- (14) Two-stage vapor condenser with steam jet ejectors (PH-XII).
- (15) Common vent for acetone tower and purification section of PH-XI and PH-XII of 22-1.
- (16) Up to once per year, PH-XIV of 22-1 serves as an emergency relief tank for oxidation, concentration and other sections, as well as providing normal venting from wash section; normal water level is 6 foot depth.
- (17) Cumyl phenol and phenolic tar (60 wt. %), acetophenone (30 wt. %) and phenol (8 wt. %) liquid stream burned at rate shown about 12 times a year for 14 hours each time, for a total of 500,000 lbs./year.
- (18) Flow of 16,500 SCFM for PH-XV of 22-8 assumes design operation of two identical burners in parallel with 100% excess O₂, together with steam injection rate of 2 lbs. steam/lb. of hydrocarbon fuel, using 10,000 SCFH fuel gas and 10,000 lb./hr. steam while flare is being operated to burn liquid waste.

TABLE PH-V
NUMBER OF NEW PLANTS FY 1980
CAPACITIES MM LBS./YR.

Current Capacity	Marginal Capacity	Current Capacity On-stream in 1980	Demand 1980	Capacity 1980	Capacity to be added by 1980	Plant Size	Number of New Units
2,363 (a)	233 (b)	2,130	3,800	4,200	2,070 (c)	200	10 - 11

Notes:

- (a) See Section VI, Phenol Producers, for source.
- (b) Arbitrary 50% of 1972 non-cumene and smaller plants.
- (c) Including replacement for marginal capacity.

TABLE PH-VI
EMISSION SOURCE SUMMARY
TON/TON OF PHENOL PRODUCT

Emissions	Source				Total
	Location in Plant	Oxidation Section	Concentration Cleavage Section	Distillation Section	Fugitive Emissions
Hydrocarbons		.0038	.0021	.0038	.0006
Particulates & Aerosols		None	None	None	None
NO _x		None	None	None	None
SO _x		None	None	None	None
CO		None	None	None	None

TABLE PH-VII
WEIGHTED EMISSION RATES

Chemical	Phenol				
Process	Air Oxidation of Cumene				
Increased Capacity by 1980 2,070 MM Lbs./Yr.					
Pollutant	Current Capacity Emissions, Lb./Lb.	Projected New Capacity Increased Emissions MM Lbs./Yr.	Weighting Factor	Projected New Capacity Weighted Emissions MM Lbs./Yr.	
Hydrocarbons	.0103	21.3	80	1,704	
Particulates	0		60		
NO _x	0		40		
SO _x	0		20		
CO	0		1		

Significant Emission Index = 1,704 MM Lbs./Yr.

TABLE PH-VIII - REFERENCES

- i P. W. Sherwood, *Pet. Proc.* 8, p 1348 (September, 1953).
- ii J. Gordon, *Hydr. Proc. & Pet. Ref.* 40, p 193 (June, 1961).
- iii M. Sittig, " " " " 41, p 129 (August, 1962).
- iv R. B. Stobaugh, *Hydr. Proc.* 45, p 143 (January, 1966).
- v Kirk-Othmer, 2nd Ed. Vol. 15, p 147 (1968).
- vi Processes Research, Inc. Task Order No. 14. Final Report Air Pollution Control in Phenol Industry (8/13/71).
- vii Chemical Profile, Chemical Marketing Reporter "Phenol", (6/19/72).
- viii J. L. Blackford "Chemical Economics Handbook", Stanford Research Institute, (July, 1972).
- ix G. P. Armstrong, et al *J. Chem. Soc.* p 666 (1950).
- x A. C. Davies, et al " " " p 2204 (1954).
- xi M. Bassey, et al " " " p 2471 (1955).
- xii Alwyn C. Davies, "Organic Peroxides" Butterworths, London (1961).
- xiii P. Gray & A. Williams. *Chem. Reviews* 59, p 239 (1959).
- xiv Perry "Chemical Engineers Handbook, 4th Ed., Mc Graw Hill (1969).
- xv S. W. Benson, et al. "Additivity Rules for the Estimation of Thermochemical Properties", *Chem. Reviews* 69, p. 279 - 324 (1969).

High Density Polyethylene

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	HP-1
II. Process Description	HP-2
III. Plant Emissions	HP-3
IV. Emission Control	HP-6
V. Significance of Pollution	HP-7
VI. HDPE Producers	HP-8

List of Illustrations & Tables

Flow Diagram	Figure HD-I
Net Material Balance	Table HP-I
Gross Heat Balance	Table HP-II
Emission Inventory	Table HP-III
Catalog of Emission Control Devices	Table HP-IV
Number of New Plants by 1980	Table HP-V
Emission Source Summary	Table HP-VI
Weighted Emission Rates	Table HP-VII

I. Introduction

More polyethylene is produced in the United States than any other plastic. Several types of polyethylene are produced. The two most important basic types are High Density Polyethylene (HDPE) - the subject of this survey report - Low Density Polyethylene (LDPE). HDPE currently holds roughly one-third of the total polyethylene market; however, due to a higher predicted growth rate, it is expected to significantly increase its share of the market by 1980. The major portion of the noxious emissions resulting from the production of HDPE is related to the separation and repurification of solvents and unreacted monomers from the virgin polymer. Significant emissions may also emanate from the pneumatic conveyor vent system - the pneumatic conveyors being used to transport the HDPE granules to various blending and storage facilities. In addition the the vapor emissions, waste water, spent catalysts and off-spec HDPE are 'produced' and must be disposed of by the operator. Also some plants produce a relatively low molecular weight 'wax' which, if incinerated, would add to the volume of air emissions.

There are three basic types of process, namely solution, slurry and vapor phase. The slurry process, as licensed by Phillips, accounts for most of today's capacity and as such is the primary subject of this report. Union Carbide is now offering licenses on a vapor phase process but none is yet in operation in the U.S. Total U.S. capacity for HDPE is expected to reach 8.5 billion pounds by 1980.

II. Process Description

Any description of current commercial ethylene polymerization techniques/processes will necessarily be quite sketchy since the details of these processes are closely guarded trade secrets. Hence, the following section is more abbreviated than in most of the survey reports.

There is great variety in the various HDPE processes utilized today. Processes of similar design may be grouped together if classification is determined by the types of phases present in the polymerization reactor. Accordingly, there are three major categories: (1) solution, (2) slurry, and (3) vapor phase. These categories may be further subdivided according to the physical state of the catalyst, but that detail will not be discussed here. The solution process is thought by many to be on the way out. Union Carbide has recently shut down the solution line at its Seadrift, Texas plant. The vapor phase process, may be of more importance in the future. The slurry process, as exemplified by Phillips Particle Form (PF) process, accounts for the bulk of the HDPE produced in the U.S. Indeed, Phillips claim (1) that their process accounts for more HDPE capacity in the U.S. than all other processes combined. Consequently, this process description will confine itself to that variation.

The mechanism of ethylene polymerization on a metal oxide surface - Phillips uses a chromic oxide catalyst - is quite complex (2). The simplified net reaction is:



The ethylene feed plus any co-monomer are treated to remove catalyst poisons; primarily CO₂, O₂, and H₂O; prior to their dissolution in an appropriate solvent - such as pentane. The solution of monomers and pentane is then heated and pumped to a bank of stirred or loop-type reactors, where it is mixed with a previously activated, powdered catalyst that has been slurried in the C₅ solvent. The monomers polymerize around the fine catalyst particles, which are kept in suspension by agitation. The heat of polymerization is absorbed by the water-cooled reactor jacketing. Polymer molecular weight or chain length is controlled by the addition of small amounts of hydrogen or other telogens.

After a suitable residence time in the reactor, the effluent slurry is pumped (continuously or batch-wise) to the 'flash' section where part of the solvent, unreacted monomers, oligomers-'waxes', and light gases are flashed overhead. The flash gases are separated and purified, with the solvent and monomers being recycled. The 'waxes' are rejected and incinerated or disposed of in some other manner.

The HDPE 'granules' may be dissolved in hot solvent and the catalyst particles filtered out, however, it is believed that current practice is to allow the small amount of catalyst now required for polymerization to remain in the HDPE. Then the polymer is stripped of the remaining solvent, dried and conveyed to a blending or storage area.

(1) C.W. 5/10/72, pp 42.

(2) See "Crystalline Olefin Polymers" - Part I by Raff & Doak for discussion.

III. Plant Emissions

A. Continuous Air Emissions

1. Flue Gas

Two operators (EPA Code No 24-10 and 24-9) report using natural gas as fuel. Operator 24-9 specifies that the fuel is used in a catalyst activation heater. The amounts of fuel; 6 and 40 mm scf/year, respectively; and the quantity of sulfur, 1 to 3 ppm, are such that SO₂ emissions are negligible.

2. Monomer and Solvent Recovery Vents

All producers recycle solvent and most recycle unreacted monomer. These recycled streams require purification. The light and heavy ends from the purification process are either vented, flared, or sent to another process or a pollution control device. This operation is one of the main sources of air pollution in the production of HDPE. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

3. Conveyor Losses

Semi-finished and finished HDPE granules are transported in-plant via pneumatic conveyors, by at least one operator (EPA Code No. 24-9). The various atmospheric vents that are associated with such a system are a source of hydrocarbon and particulate emissions. These emissions represent a significant portion of the total emissions despite employment of various pollution control devices. The emission and device data are summarized in Tables III and IV.

B. Intermittent Air Emissions

1. Catalyst Activation

The Phillips type catalysts require activation prior to use. Activation is accomplished by blowing hot air over/through the catalyst. Operator EPA Code No. 24-9 states that this is a batch-type operation. The emissions resulting from this operation are listed in Table III.

2. Feed Treatment

Polar substances poison Phillips type catalysts; consequently, water must be removed from the feed. This is accomplished through the use of mole sieve absorbers. The absorbers are periodically regenerated and eventually dumped. During these operations the vessels are purged with the vent stream blowing to the atmosphere. These relatively small emissions are summarized in Table III.

3. Reactor Catalyst Charging/Dumping

One operator (EPA Code No. 24-1) who uses a supported Zeigler type catalyst reports weekly emissions of a nitrogen-alumina stream. This apparently occurs during catalyst dumping operations, but it is not perfectly clear. The emissions resulting from this operation are summarized in Table IV.

4. Start-Up and Emergency Vents

This type of discharge is universally encountered in the petrochemical industry and will vary from process-to-process, from operator-to-operator, and from year-to-year. According to the responses received to the HDPE questionnaires, all of these vents are flared. This need not necessarily be the case for the entire industry but since they are primarily hydrocarbon streams, it is probable that they are flared.

Flaring is a very effective method of reducing air pollution, especially in situations such as this where the only products of complete combustion are carbon dioxide and water. The only problem with flares is that they must have a finite design limitation, beyond which they will not achieve complete combustion and thus are no longer "smokeless". In extreme emergencies they are apt to receive entrained liquids or excessive gas flows, resulting in smoky effluents.

One respondent (EPA Code 24-9) reported the smokeless design rate at 122,900 lbs./hour. This is nearly five times their hourly production rate of polyethylene so it is probably an adequate safety margin for most situations. However, the solvent circulation rate is probably six or more times the production rate and vessel capacities are even a greater multiple of capacity, therefore, it is possible that some smoky flare conditions could be encountered.

One additional point, about which all respondents were silent is NO_x . The reaction between atmospheric nitrogen and oxygen is known to produce these pollutants at high temperatures. Hence, it is probable that some small concentration of NO_x is produced in the flame.

C. Liquid Wastes

The only liquid waste reported was water. Operator EPA Code No. 24-10 reported discharging 330 gpm of waste water. Operator EPA Code No. 24-9 reported discharging 100 to 150 gpm of water after primary treatment. It was stated that this water was used for cooling and as a HDPE pellet transfer medium. Operator EPA Code No. 24-1 reported a waste water stream of 1000 gph containing 15 ppm cyclohexane. This concentration of cyclohexane represents $<.000001$ ton/ton of HDPE.

D. Solid Wastes

1. Spent Catalysts

Depending on the process used, catalyst may or may not be removed from the polymer. One operator who obviously does remove it (EPA Code No. 24-1) reports the disposal of 1×10^6 lbs./yr. of this material. It is hauled away by a waste disposal contractor.

2. Polyethylene Waste

The amount of non-specification HDPE produced is a function of the process used, the stringency of product molecular weight

range specifications, and many other factors. The actual amount reported varied from 2×10^5 to 2×10^6 lbs./yr. Some of this material may be applied in lower specification uses, but the remainder is either incinerated or removed by contract haulage.

3. Waxes

Varying amounts of relatively low molecular weight 'waxes' are produced by most HDPE processes. One operator (EPA Code No. 24-1) reported that 2×10^5 lbs./yr. are produced and disposed of by a contractor. Another operator (Code 24-10) reports "considerably less" than this amount.

E. Odors

No odors are reported by any of the questionnaire respondents. However, many of the reported vent streams contain materials that have odors.

F. Fugitive Emissions

Two of the four respondents reported fugitive emissions, both of fairly significant proportions, as follows:

Code 24-10 "Assuming 50% of unaccounted for non-methane hydrocarbons to flare and 50% to atmosphere - 5,900 tons/year fugitive loss".

Code 24-4 "Fugitive losses amounting to 7 MM lbs./year occur. These include ethylene, butene, cyclohexane, pentane and iso-butane and are equivalent to 0.5% of throughput."

These are each of the order of 0.03 lbs./lb. of product and thus are significant, being about equal to the total of all other reported hydrocarbon emissions. Yet, the other respondent reports no fugitive emissions, "other than small leaks".

Two rather obvious questions occur as a result of these reports, namely:

Are these estimates of losses real or can they be attributed to metering inaccuracies or material balance non-closure caused by small differences between very large members?

If these losses are real, are they air emissions or do most of them enter the flare header because of leaking relief valves?

It is assumed that the losses are in fact atmospheric emissions resulting and are of the order of 200 SCFM per plant.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of high density polyethylene plants are summarized in the Catalog of Emission Control Devices - Table IV. In general, no quantitative information on the device performance has been made available. (In some instances, approximate numerical efficiencies have been assigned to these devices, see Table IV - on the basis of the operator's estimate of effluent composition). Never-the-less, certain generalizations about the performance of the devices utilized can be made:

Water Scrubbers

Only one water scrubber was reported as being used. That is, operator EPA Code No. 24-1's device HP-2, which is used to remove "small quantities of alumina dust" from the exhaust gases of a reactor vent cyclone during weekly catalyst transferrals. The effluent from the device is described as being "essentially dust free". Since the device in question is a multi-tray scrubber working on what may be assumed to be a stream only lightly laden with particulate matter; its efficiency should be reasonably high. However, it would be imprudent to attempt to characterize the performance of all the scrubbers used by the industry on the basis of that single report.

Cyclones

In high density polyethylene production these devices are used to remove or reduce the amount of HDPE dust emitted from the pneumatic conveyor vent system. The size of the particles being removed is reported as varying from 10 to 150 microns. The device efficiencies cannot be calculated from the data reported; but one may infer, from the variations in the description of cyclone exhaust gases, that there are significant differences in the performances of existing equipment. For example the operator of device HP-1 reports that the effluent from that device is "essentially dust free", whereas the operator of device HP-7a states that there are visible particulate emissions exhausting from it. The operator of device HP-7a (Plant EPA Code No. 24-9) further states that the currently existing cyclones will be replaced in the future - with higher efficiency cyclones and bag filters.

Bag Filters

In general, bag filters are utilized for the same type of service as cyclones. The single exception is device HP-5 which is used by the operator of plant EPA Code No. 24-9 to remove catalyst fines from the atmospheric vent stream resulting from catalyst activation operations. The device is reported to remove all of the 10 to 200 micron particles which comprise its (particulate) feed.

Bag filters, when used to service pneumatic conveyor vent streams, apparently exhibit the same variation in performance that was reported for cyclones. Descriptions of filter exhaust streams range from "no particulates" to "visible (particulate) emissions". Unfortunately more quantitative data are lacking. Operator EPA Code No. 24-9 states that single compartment bag filters used in this service will be replaced with more efficient multi-compartment bag filters.

Incinerators & Flares

All HDPE plant operators report the employment of a flare system. Again, the data necessary to calculate efficiencies have not been reported. Where

specified, all flares are associated with the reactor section. Only one plant operator, (EPA Code No. 24-1) reports incinerating off-spec HDPE. No details are given as to the type of incineration used or the amount of HDPE incinerated, except that the total amount of off-spec HDPE produced is 2×10^5 lbs./yr. with a part being incinerated and part removed by a solid waste disposal contractor.

Possible Methods for Emission Reduction

It seems unlikely that any change in operating conditions could be made within a given process, that would reduce air emissions without affecting various product qualities. However, it is conceivable that the choice of solvents could have a significant effect in overall emissions. Additionally, catalysts (or processes) that produce less 'wax' and off-spec HDPE will lessen pollution resulting from the production of HDPE.

Development work directed toward reductions in emissions from this process falls into the following general categories:

- (1) Design and utilization of closed-loop pneumatic conveying systems, i.e., no atmospheric vents.
- (2) Development of catalysts that produce no wax and minimize off-spec HDPE.
- (3) Determination of solvent system that reduces emissions without adversely affecting the HDPE quality.
- (4) Controlled combustion of hydrocarbon vent streams to minimize formation of NO_x and to recover heat, where justified.

V. Significance of Pollution

It is recommended that an in-depth study of this process be undertaken. Both the growth rate and quantity of pollutants emitted to the atmosphere are significant.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

The Table V forecast of new plants is based on the assumption that the HDPE growth experienced from 1965 to 1972 will extend to 1980. This is supported in part by the forecast in the final report, task order No. 15, page B-12, prepared for the EPA by Process Research, Incorporated. On the other hand Chemical Marketing of January 18, 1971, predicts a growth rate of 10% per year until 1975. If this rate were extrapolated to 1980, HDPE capacity at that time would be only 60% of the rate that Table V is based on. Obviously, there are serious differences of opinion on the future of HDPE.

A Significant Emissions Index (SEI) of 17,196 has been calculated in Table VII. However, as explained above, the basis for the SEI calculation, i.e., the 1980 capacity is subject to question. Furthermore, more than half of the total SEI is attributable to "fugitive emissions", yet some respondents have reported only minimal losses in this category. It is only by means of an in-depth study that these uncertainties can be clarified and the need for new source standards evaluated. Hence, the recommendation for such a study has been made.

VI. High Density Polyethylene Producers

The following tabulation of producers of high density polyethylene indicates published capacity:

<u>Company</u>	<u>Location</u>	<u>Capacity MM Lbs./Yr.</u>
Allied Chemical Corp.	Baton Rouge, La.	225
Amoco Chemicals Corp.	Chocolate Bayou, Texas	100
Celanese Corporation	Deer Park, Texas	225
Chemplex Co.	Clinton, Iowa	125
Dow Chemical Co.	Freeport, Texas Plaquemine, La.	100 100
E. I. DuPont deNemours & Company	Orange, Texas	180
Gulf Oil Corporation	Orange, Texas	100
Hercules, Inc.	Lake Charles, La.	90
Monsanto Company	Texas City, Texas	180
National Petro Chemicals Corporation	La Porte, Texas	220
Phillips Petroleum Co.	Pasadena, Texas	300
Sinclair-Koppers Co.	Port Arthur, Texas	200
Union Carbide	Seadrift, Texas	<u>140</u>
Total -		2,315

157

TABLE HP-1
TYPICAL* HIGH DENSITY POLYETHYLENE UNIT
MATERIAL BALANCE, T/T OF HDPE

Stream No.	1	2	3	4	5	6	7	8	9	10
	Fresh Feed	Make-up Solvent	Catalyst	Recycle	Gross Reactor** Feed	Reactor Effluent	Solvent Recovery Vent & Losses	Heavy Reject	HDPE Handling Losses	Product
Ethylene	1.0156			0.1144	1.1300	0.1147	0.0003			
Butene-1	0.0086			0.0258	0.0344	0.0258				
Polyethylene						1.0010			0.0010	1.0000
Solvent		.0340		5.6999	5.7339	5.7339	.0340	0.0229		
Low M. Wt. 'wax'			.000002			0.0229		0.0229		
Catalyst										
	1.0242	.0340	.000002	5.8401	6.8983	6.8983	.0343	.0229	.0010	1.0000

*No single material balance can be truly typical of the various processes used to produce HDPE. The above balance is an approximation (from sparse published data) of the Phillips Suspension Process which has been represented** as the process accounting for the major portion of HDPE capacity in the U. S. today.

**C.W. 5-10-72, pp 41

***There is considerable variation in the solvent/ethylene ratio reported in the literature. It is possible that it is considerably higher than shown in the material balance.

TABLE HP-II
HIGH DENSITY POLYETHYLENE
VIA
ETHYLENE POLYMERIZATION
GROSS HEAT BALANCE

The exothermic heat of ethylene homopolymerization is 1450 BTU/LB. (1) (of ethylene).

There are not sufficient published data available to permit the construction of a typical commercial reactor section gross heat balance for this process.

(1) Chem. Eng. 73 (16) 68 - August 1st, 1966.

Company
Location
EPA Code No.
Capacity - Tons of H.D. Polyethylene/Yr.
Average Production - Tons of H.D. P. E./Yr.
Range in Production - % of Max.
Emissions to Atmosphere
Stream

Flow - lb./hr.
Flow Characteristic - Continuous or Intermittent
if Intermittent - hrs./Yr. Flow
Composition - Ton/Ton of H.D. P.E.

Hydrogen
Ethylene
Butene
Isobutane
Isopentane
Hexene
Polyethylene
Cyclohexane
Air
Alumina
Co-Monomers

Sample Tap Location
Date or Frequency of Sampling
Type of Analysis
Odor Problem

Vent Stacks

Flow SCFM per stack

Number

Height - Feet

Diameter - Inches

Exit Gas Temperature - °F

Emission Control Device

Type - Flare

Bag House

Cyclone

Water Scrubber

Other

Catalog I. D. Number

Total Hydrocarbon Emissions - ton/ton H.D. P. E.

Total Particulate - ton/ton

Total SO_x - ton/ton

Total NO_x - ton/ton

Total CO - ton/ton

TABLE HP-III
NATIONAL EMISSIONS INVENTORY
HIGH DENSITY POLYETHYLENE PRODUCTION

Page 1 of 3

P. E. Stripping & Blending Vent	Reactor Vent	Emergency Vent ex. Distillation	Equip. Purge & Emergency Vent ex. Compress Sect.	Equip. Purge & Emergency Vent ex. Reactor Sect.	Equip. Purge & Emergency Vent ex. Polymer Recovery Section
200,400 Continuous	3,540 Intermittent 1,250	Not Specified Intermittent (3 min/incident)	Not Specified Intermittent Not Specified	Not Specified Intermittent Not Specified	Not Specified Intermittent Not Specified
		+	+	+	+
.01768 8.83978	+		+	+	+
		+	+	+	+
Up-stream of HP-1 Continuous "Flammability" anal	None Not Sampled	None Not Sampled	None Not Sampled	None Not Sampled	None Not Sampled
No	No	No	No	No	No
Not Specified	Not Specified		Yes		
Yes	Yes		1		
			235		
			30		
			Not Specified		
			Yes		
			X		
"Dust Precipitator"	X				
HP-1	HP-2	HP-3			
	Cannot be determined but > 0.1768				
	Cannot be determined				
	" "				
	" "				
	" "				
	" "				

TABLE HP-III
NATIONAL EMISSIONS INVENTORY
HIGH DENSITY POLYETHYLENE PRODUCTION

Page 2 of 5

Company Location EPA Code Number		24-9 110,000 103,500 0	Feed Prep Section Purge Not Specified Intermittent Not Specified	Solvent Recov. Section Purge Not Specified Intermittent Not Specified	Emergency Vent ex. Reactor 80,000 Intermittent (15 min/incident)	Emergency Vent ex. Solvent Process 200-1500 Intermittent Not Specified
Capacity - Tons of H.D. Polyethylene/Yr. Average Production - Tons of H.D. P.E./Yr. Range in Production - % of Max. Emissions to Atmosphere Stream						
Flow - lb./hr. Flow Characteristic - Continuous or Intermittent if Intermittent - hrs./yr. flow						
Composition - ton/ton of H.D. P.E.						
Hydrogen		+			+	+
Ethylene		+			+	+
Butene		+			+	+
Isobutene		+			+	+
Isopentane		+			+	+
Hexane		+			+	+
Polyethylene						
Cyclohexane						
Air						
Alumina						
Co-Monomer		+				+
Nitrogen		+				
Fuel Gas						
Silica Gel						
Sample Tap Location						
Date or Frequency of Sampling						
Type of Analysis						
Odor Problem						
Vent Stacks						
Flow SCFM per stack						
Number						
Height - Feet						
Diameter - Inches						
Exit Gas Temperature - °F						
Emission Control Devices						
Type - Flare						
Bag House						
Cyclone						
Water Scrubber						
Other						
Catalog I. D. Number						
Total Hydrocarbon Emissions - ton/ton HDPE						
Total Particulate - ton/ton HDPE						
Total NO _x Emissions ton/ton HDPE						
Total SO _x Emissions ton/ton HDPE						
Total CO Emissions ton/ton HDPE						
Not Sampled						
Mat'l Bal.						
No						
Yes						
Not Specified						
1						
150						
Yes						
+						
HP-4						
See Continuation of This Table						

TABLE HP-III
NATIONAL EMISSIONS INVENTORY
HIGH DENSITY POLYETHYLENE PRODUCTION

Page 3 of 5

24-9 110,000 103,500 0			
Catalyst Activation Section Vent 200 Continuous Downstream of HP-5	HDPE Conveying ex. Blending Vent 42,172 (A) Continuous Downstream of HP-6	Intermed. Ste. Conveying Vent 6800 (C) Continuous Downstream of HP-7	Packaging Conveyor 96,400 (E) Continuous Downstream of HP-8
.00850	+	+	+
	(Total) 1.79280	(Total) .27200	(Total) 3.85000
+	Not Sampled	Not Sampled	Not Sampled
Mat'l Bal.	Mat'l Bal.	Mat'l Bal.	Mat'l Bal.
No	No	No	No
Not Specified	Not Specified	Not Specified	Not Specified
Yes	Yes	Yes	Yes
+	+	+	+
HP-5	HP-6 (B)	HP-7 (D)	HP-8 (F)

.035564

Company
Location
EPA Code Number
Capacity - Tons of H.D. Polyethylene/Yr.
Average Production - Tons of H.D. P.E./Yr.
Range in Production - % of Max.
Emissions to Atmosphere
Stream
Flow - lb./hr.
Flow Characteristic - Continuous or Intermittent
if Intermittent - hrs./yr. flow
Composition - ton/ton of H.D. P.E.
Hydrogen
Ethylene
Butene
Isobutane
Isopentane
Hexene
Polyethylene
Cyclohexane
Air
Alumina
Co-Monomer
Nitrogen
Fuel Gas
Silica Gel
Sample Tap Location
Date or Frequency of Sampling
Type of Analysis
Odor Problem
Vent Stacks
Flow SCFH per stack
Number
Height - Feet
Diameter - Inches
Exit Gas Temperature - F°
Emission Control Devices
Type - Flame
Bag House
Cyclone
Water Scrubber
Other
Catalog I. D. Number
Total Hydrocarbon Emissions - ton/ton HDPE
Total Particulate - ton/ton HDPE
Total SO_x Emissions ton/ton HDPE
Total NO_x Emissions ton/ton HDPE
Total CO Emissions ton/ton HDPE

10

163

TABLE HP-III
EXPLANATION OF NOTES
NATIONAL EMISSIONS INVENTORY
HIGH DENSITY POLYETHYLENE PRODUCTION

Page 5 of 5

<u>Note</u>	<u>Comment</u>
A	Total maximum flow for four separate streams.
B	Device HP-6 consists of 14 separate bag filters with an average of four compartments per filter and 15 bags per compartment.
C	Reported data interpreted as meaning stated flow is total for eight separate streams.
D	Device HP-7 consists of 34 cyclones and 11 bag filters. Table IV lists the cyclones under HP-7a and the bag filters under HP-7b.
E	Reported data interpreted as meaning stated flow is total for four separate streams.
F	Device HP-8 consists of four cyclones.
G	Respondent has verbally reported that his conveyor emission factors are comparable to those reported by respondent 24-10.

FLARE SYSTEM

Flow Diagram Stream I, D, Letter
 Device I, D, Number
 EPA Code No. for plant using
 Types of compounds incinerated
 Amount incinerated - lb./hr. (SCPM)
 Device or stack height - ft.
 Stack diameter @ tip - inches
 Installed Cost - Mat'l & Labor - \$
 Operating Cost - Annual - \$
 Efficiency (V) GPH -
 Efficiency (V) SEER -

WATER SCRUBBERS - Device I, D, Number

Flow Diagram Stream I, D, Letter
 EPA Code No. for plant using
 Purpose - Control emission of
 Type - Spray
 Packed column
 Trays - Type
 Number
 Plenum chamber
 Other
 Water rate - GPM
 Design (operating) Temp. - $^{\circ}$ F
 Gas Rate - SCFM
 TI - Height - ft.
 Diameter - ft.
 Installed Cost - Mat'l & Labor, \$
 Operating Cost - Annual - \$
 Efficiency (V) GPH -
 Efficiency (V) SEER -

TABLE HP-IV
 CATALOG OF EMISSION CONTROL DEVICES
 HIGH DENSITY POLYETHYLENE

Page 1 of 1

Emission Section		
(B) HP-3 24-1 Various lt. H.C. 235 30 76,000 .04199 5,000 .00276	(B) HP-4 24-9 Various lt. H.C. 150 22,600 .01092 12,250 .00592	(B) HP-10 24-1 Various lt. H.C. 100 16 9,500 .00315 26,500 .00878
HP-2 (B) 24-1 Alumina dust X X 10 800 12.75 2 20,000 .01105 4,000 .00221		HP-10 24-1 Various lt. H.C. 100 16 9,500 .00315 26,500 .00878

BAU FILTERS

Flow Diagram Stream I, D, Letter
 Device I, D, Number
 EPA Code No. for plant using
 Purpose - control emission of
 Number of compartments
 Bags per compartment
 Type cloth used for bags
 Total bag area - ft²
 Design (operating) temp - F°
 Design (operating) pressure - PSIG
 Installed Cost - Mat'l & Labor - \$
 Operating Cost - Annual - \$
 Efficiency - %

CYCLONES

Flow Diagram Stream I, D, Letter
 Device I, D, Number
 EPA Code No. for plant using
 Purpose - control emission of
 TI - Height - Ft.
 Diameter - Ft.
 No. of Stages
 Installed Cost - Mat'l & Labor - \$
 Operating Cost - Annual - \$
 Efficiency

TABLE HP-IV
 CATALOG OF EMISSION CONTROL DEVICES
 HIGH DENSITY POLYETHYLENE

Page 2 of 3

Catalyst Activation Section	Reactor Section	HDPE Stripping & Blending Sect.	Product Conveying Vent	Product Packaging Vent
(A) HP-5 24-9 Catalyst Dust 1	(C) HP-6 (I) 24-9 HDPE Dust 4 15	(D) HP-7b (II) 24-9 HDPE Dust Not Specified	(E) HP-8 (IV) 24-9 HDPE Dust Not Specified	(F) HP-8 (IV) 24-9 HDPE Dust Not Specified
Orlon 200 250 3640 00176 250 00012 100	(Total) 101,000 (Total) .04879 (Total) 3,500 (Total) .00169 100	(Total) 31,800 (Total) .01536 0 0	(Total) 9,700 (Total) .00469 (Total) 1,500 (Total) .00073 ~100'	
	(C) HP-1 24-1 HDPE Dust Not Specified	(D) HP-7a (III) 24-9 HDPE Dust 5 1.8 1 (Total) 43,200 (Total) .02087 0 0 ~100 (on particulates)		
	30,000 .01658 6,000 .00332 ~100 (on particulates)			

TABLE HP-IV
EXPLANATION OF NOTES
CATALOG OF EMISSION CONTROL DEVICES
HIGH DENSITY POLYETHYLENE PRODUCTION

Page 3 of 3

<u>Note</u>	<u>Comment</u>
I	Device HP-6 consists of 14 separate bag filters with an average of four compartments/filter and 15 bags/compartment.
II	Device HP-7b consists of 11 individual bag filters.
III	Device HP-7b consists of 34 individual cyclones.
IV	Device HP-8 consists of four separate cyclones.
V	See Appendix V of this report for explanation of CCR and SERR efficiencies.

TABLE HP-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980*	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
2,315	0	2,315	8,500	8,500	6,186	200	30 - 31

NOTE: All capacities in MM lbs./yr.

*1980 demand based on Stanford Research Institute's 'Chemical Economics Handbook', Section 580.1330.

See also discussion on page HP-8.

TABLE HP-VI
EMISSION SOURCE SUMMARY*
TON/TON HDPE

Emissions	Source						Total
	Catalyst Prep.	Reactor	Solvent Recovery	Polymer Stripping	Product Conveying	Fugitive	Flare
Hydrocarbons			.0020	.0090	.0030	.0200	.0340
Particulates					.0010		.0010
NO _x	Negligible	Negligible					0
SO _x							0
CO							0

*All quantities used in this table are based on data reported in questionnaires from plants with EPA Code Nos. 20-0, 20-1, 20-4, and 20-9. Most numbers have been subject to some adjustment - as dictated by the demands of engineering judgement.

TABLE HP-VII
WEIGHTED EMISSIONS RATES

Chemical High Density Polyethylene

Process Intermediate and Low Pressure Polymerization

Increased Capacity by 1980 6,185 MM Lbs./Year

Pollutant	Emissions, Lbs./lb.	Increased Emissions MM Lbs./Year	Weighting Factors	Weighted Emissions MM Lbs./Year
Hydrocarbons	.034	210.3	80	16,824
Particulates	.001	6.2	60	372
NO _x	TR	TR	40	TR
SO _x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 17,196 (MM lbs./yr.)

Low Density Polyethylene

Table of Contents

<u>Section</u>	<u>Page Number</u>
I. Introduction	LP-1
II. Process Description	LP-2
III. Plant Emissions	LP-3
IV. Emission Control	LP-5
V. Significance of Pollution	LP-6
VI. LDPE Producers	LP-7

List of Illustrations & Tables

Net Material Balance	Table LP-I
Gross Heat Balance	Table LP-II
National Emissions Inventory	Table LP-III
Catalog of Emission Control Devices	Table LP-IV
Number of New Plants by 1980	Table LP-V
Emissions Source Summary	Table LP-VI
Weighted Emission Rates	Table LP-VII
Flow Diagram	Figure LD-1

1. Introduction

More polyethylene is produced in the United States than any other plastic. Several types of polyethylene are produced. The two most important types are High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE). The screening effort in this report is based on questionnaires returned by seven LDPE manufacturers.

As of January, 1971, approximately 5,300,000,000 lbs./year of LDPE capacity existed in domestic facilities. Emissions arising from these facilities come primarily from materials handling; purges and venting of equipment and lines; gas separation and other recovery operations; and fugitive emissions. The pollutants are predominantly hydrocarbon vapors and fine polymer particulates. Relative to pollution significance, LDPE projections to the year 1980 indicate an SEI* of about 21,300. This index rating places LDPE in the ranks of petrochemicals which qualify for in-depth studies.

Note: Questionnaire response Code No. 24-8 came to review status just prior to issuance of this screening report. Therefore, the information in response 24-8 does not participate in the detailed structuring of this report. It can be stated, however, that - except for minor nuances such as in emission stream component concentrations - the 24-8 report content in general, fits the pattern of previous reports on LDPE.

*See Appendix IV for explanation.

II. Process Description

This is a simplified description of a modern high pressure ethylene polymerization process for the production of low density polyethylene (LDPE). A detailed technological description is 1) not necessary to fulfill the objectives of this screening report, and 2) not possible from information currently available in published form.

A simplified composite flow diagram is attached. Please see fold-out Drawing No. R-209. (Figure LD-I)

The characterizing variable in the LDPE reaction is pressure, which normally ranges from 10,000 to 30,000 PSIG, and can reach levels as high as 45,000 PSIG. The mechanism of ethylene polymerization on the catalyst surface is quite complex. The simplified net reaction:



R_1 and R_2 represent chain-terminations resulting from the introduction of "telogens" specifically chosen to accomplish this end. (Although not shown above, LDPE polymer structures are usually characterized by branched chains.) The ethylene monomer polymerizes in a stirred autoclave or a tubular reactor. During the reaction sequence, temperature is controlled at predetermined levels by a heat transfer system which can add or remove heat in exact accord with processing requirements. (Copolymers and other variations are commercially important; e.g., the vinyl acetate copolymer, "EVA".)

After a suitable residence time in the reactor, the monomer-polymer mix continues to the flash section where unreacted monomers and some "waxy" material are flashed overhead. The flash vapor components are separated and purified. Recovered monomers are recycled, and the waxy materials are buried, incinerated or handled by some other suitable means of disposal.

The crude LDPE is extruded and pelletized (or otherwise mechanically prepared) so that it can be fed to the materials handling and finishing system which follows.

The most common form of materials handling system for the pellets is airveying. This type of system permits intermediate and pre-shipment storage in an effectively **deployed** network of silos.

III. Plant Emissions

A. Continuous Air Emissions

1. Flue Gas

No process fuel usage is reported.

2. Purification and Recovery Vents

All producers recycle unreacted monomer. The recovery streams require purification. The light and heavy ends from the purification process are either vented, flared, sent to another process, or to a pollution control device. These operations can be one of the sources of air pollution in the production of LDPE. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

3. Materials Handling Losses

Semi-finished and finished LDPE granules are most often transported in-plant via pneumatic conveying systems. The various atmospheric vents that are associated with these systems are a source of hydrocarbon and particulate emissions. The hydrocarbon content of these emissions arises from a significant monomeric ethylene residual in the pellets. The ethylene diffuses from the pellets into the conveying air and silo purge air. Continuous particulate emissions are presumed not significant with suitable retention means such as cyclones and bag filters. Emission and control device data are summarized in Tables III and IV.

B. Intermittent Air Emissions

1. Catalyst Activation, Feed Treatment and Reactor Charging and Dumping

These operations are accompanied by significant intermittent emissions in the case of high density polyethylene production. These categories of operations are, therefore, mentioned here and are excluded as significant intermittent emissions sources in the case of LDPE production.

2. Start-Up and Emergency Vents

According to the responses received to the LDPE questionnaires, these vents are normally tied into flare systems. The products of combustion are carbon dioxide and water, except in certain emergencies when the flares receive entrained liquids or excessive gas flows, and may briefly show smoky effluents.

The LDPE respondents' reports indicate that smokeless flare designs contain adequate safety margin for most situations. However, extreme swings in design parameters occasionally lead to upset conditions; e.g., pilot flame-out; excessive turndown demands; low or zero steam pressure.

NO_x formation resulting from the above start-up and emergency vent

flaring is not considered appreciable, relative to the national emissions inventory.

C. Waste Water

Water is used in the extrusion steps for cooling; as a pellet transfer medium; and as a means of "floating" oily liquids. However, no waste water was reported by any respondent.

D. Solid Wastes

1. Spent Catalysts

In contrast to HDPE operations, LDPE catalyst does not pose a solid waste problem.

2. Polyethylene Waste

The amount of non-specification and scrap LDPE produced is a function of the process used, the stringency of product molecular weight range specifications, and many other factors. The material is disposed of via incineration, landfill or contract haulage.

3. Waxes

Varying amounts of relatively low molecular weight solid waxes are produced by LDPE processes. Disposal is by methods similar to those employed for waste polyethylene.

E. Odors

No significant odors are reported by the questionnaire respondents. However, many of the reported vent streams contain materials that have odors.

F. Fugitive Emissions

The respondents indicate fugitive emissions (= "other emissions") of significant proportions, as shown quantitatively in the tabular portions of this report. It is assumed for the purposes of this screening study that all LDPE operations have significant fugitive emissions.

Liquid storage is 1) padded, 2) pressurized, 3) refrigerated, 4) or low volatility atmospheric tankage. The respondents are presumed to allot any liquid storage losses to "other emissions", Section VIII of the questionnaires, which they, in general, have calculated from their overall material balance.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of low density polyethylene plants are summarized in the Catalog of Emission Control Devices - Table IV. In general, no quantitative information on the device performance has been made available. Never-the-less, certain generalizations about the performance of the devices utilized can be made.

Water Scrubbers

No water scrubber or similar device was reported.

Cyclones

In low density polyethylene production, these devices are used to remove or reduce the amount of LDPE dust emitted from the pneumatic conveyor and silo vent systems. The device efficiencies cannot be calculated from the data reported. But the conclusion may be tentatively drawn that future installations may be teamed up with bag filters.

Bag Filters

Although none were reported, bag filters appear to be the ultimate final-step device for the LDPE plant of the future. A properly chosen device, according to data collected in this study and reported in Report No. EPA-450/3-006a, should remove substantially all LDPE particulate dust escaping the cyclones.

Flares & Incinerators

All LDPE plant operators are presumed to make use of a flare system. Data necessary to calculate combustion efficiencies of existing flares have not been reported. Where specified, flares are mainly associated with the purification and recovery sections. It is likely that some NO_x is formed in these flares.

Most operators are presumed to employ incinerators for the (relative small) combustible liquid waste effluents. Existing incinerators, where reported, appear to make no contribution to the national emissions inventory.

V. Significance of Pollution

It is recommended that LDPE be placed in the ranks of petrochemicals which qualify for in-depth studies. The projected LDPE capacity and the corresponding quantity of pollutants emitted to the atmosphere are significant. The significance lies principally in the large cumulative production capacity, rather than in the emissions from any single installation.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Table V, VI, and VII.

The Table V forecast of new plants is based on the assumption that the LDPE growth rate experienced from 1960 to 1969 will extend to 1980. A Significant Emissions Index (SEI) of 21,300 has been calculated. See Table VII, although the bulk of this is in the category of "fugitive emissions". This fact, along with uncertainties in the growth forecast are reasons why an in-depth study is required to determine the applicability of new source standards to the LDPE process.

VI. Low Density Polyethylene Producers

The following tabulation of producers of low density polyethylene indicates published production capacity:

<u>Company</u>	<u>Location</u>	<u>As of 1970, Installed Capacity, MM Lbs./Yr.</u>
Allied Chemical Corp.	Orange, Texas	25
Chemplex Co.	Clinton, Iowa	300
Cities Service Co.	Lake Charles, La.	220
Columbian Carbon Co.	Lake Charles, La.	220
Cosden Oil & Chemical Co.	Calumet City, Ill.	20
Dart Industries, Inc.	Odessa, Texas	365
Dow Chemical Co.	Freeport, Texas Plaquemine, La.	300 200
E. I. DuPont deNemours & Co.	Orange, Texas Victoria, Texas	425 200
Eastman Kodak Co.	Longview, Texas	250
Exxon Chemical Co. - U.S.A.	Baton Rouge, La.	330
Gulf Oil Corp.	Cedar Bayou, Texas Orange, Texas	200 300
Monsanto Co.	Texas City, Texas	140
National Distillers & Chemical Corp.	Tuscola, Ill. Deer Park, Texas	150 300
Phillips Petroleum Co.	Houston, Texas	39
Sinclair-Koppers Co.	Port Arthur, Texas	220
Union Carbide	Seadrift, Texas South Charleston, W. Va. Texas City, Texas Torrence, Calif. Whiting, Indiana	360 120 225 120 240
Total		5,269

TABLE LP-1
COMPOSITE LOW DENSITY POLYETHYLENE
NET MATERIAL BALANCE
(TONS/TON OF LDPE CAPACITY)

	Stream No. on Simplified Flow Diagram	<u>Tons/Ton LD</u>
<u>INPUT</u>		
Ethylene	1	1.0105
Catalysts	2	0.0004
Modifiers & Co-monomers*	3	0.0179
Misc. Other Additives	4	0.0071
Mineral Spirits	5	<u>0.0046</u>
Total Input		1.0405
<u>OUTPUT</u>		
Polyethylene Resin Product	6	1.0000
Waste Solids	7	0.0196
Fugitive Emissions	8	0.0100
Compressor Pot Liquids	9	0.0046
Misc. Atmospheric Vents	-	<u>0.0063</u>
Total Output		1.0405

*Including telogens (chain terminators).

**Includes vinyl acetate, propylene, iso-butane and organic peroxides.

TABLE LP-11
LOW DENSITY POLYETHYLENE
GROSS HEAT BALANCE

The exothermic heat of ethylene homopolymerization is 1450 BTU/LB. (1) of monomer.

A commercial reactor section gross heat balance for this process cannot be suitably estimated from the available published data.

(1) Chem. Eng. 73 (16) 68 - August 1st, 1966

TABLE 1B-111
NATIONAL EMISSION INVENTORY
LD DENSITY PREVENTION INFORMATION

Company	Location	EPA Code No.	Capacity - Tons of LD Polyethylene/Yr.	Average Production - Tons of LDPE/Yr.	Seasonal Range in Production - % of Max	Emissions to Atmosphere	Stream - Letter on Flow Diagram
		26-2	150,000	110,000	0	0	
		26-3	110,000	100,000	0	0	
		26-4	110,000	100,000	0	0	
		26-5	110,000	100,000	0	0	
		26-6	110,000	100,000	0	0	
		26-7	110,000	100,000	0	0	
		26-8	110,000	100,000	0	0	
		26-9	110,000	100,000	0	0	
		26-10	110,000	100,000	0	0	
		26-11	110,000	100,000	0	0	
		26-12	110,000	100,000	0	0	
		26-13	110,000	100,000	0	0	
		26-14	110,000	100,000	0	0	
		26-15	110,000	100,000	0	0	
		26-16	110,000	100,000	0	0	
		26-17	110,000	100,000	0	0	
		26-18	110,000	100,000	0	0	
		26-19	110,000	100,000	0	0	
		26-20	110,000	100,000	0	0	
		26-21	110,000	100,000	0	0	
		26-22	110,000	100,000	0	0	
		26-23	110,000	100,000	0	0	
		26-24	110,000	100,000	0	0	
		26-25	110,000	100,000	0	0	
		26-26	110,000	100,000	0	0	
		26-27	110,000	100,000	0	0	
		26-28	110,000	100,000	0	0	
		26-29	110,000	100,000	0	0	
		26-30	110,000	100,000	0	0	
		26-31	110,000	100,000	0	0	
		26-32	110,000	100,000	0	0	
		26-33	110,000	100,000	0	0	
		26-34	110,000	100,000	0	0	
		26-35	110,000	100,000	0	0	
		26-36	110,000	100,000	0	0	
		26-37	110,000	100,000	0	0	
		26-38	110,000	100,000	0	0	
		26-39	110,000	100,000	0	0	
		26-40	110,000	100,000	0	0	
		26-41	110,000	100,000	0	0	
		26-42	110,000	100,000	0	0	
		26-43	110,000	100,000	0	0	
		26-44	110,000	100,000	0	0	
		26-45	110,000	100,000	0	0	
		26-46	110,000	100,000	0	0	
		26-47	110,000	100,000	0	0	
		26-48	110,000	100,000	0	0	
		26-49	110,000	100,000	0	0	
		26-50	110,000	100,000	0	0	
		26-51	110,000	100,000	0	0	
		26-52	110,000	100,000	0	0	
		26-53	110,000	100,000	0	0	
		26-54	110,000	100,000	0	0	
		26-55	110,000	100,000	0	0	
		26-56	110,000	100,000	0	0	
		26-57	110,000	100,000	0	0	
		26-58	110,000	100,000	0	0	
		26-59	110,000	100,000	0	0	
		26-60	110,000	100,000	0	0	
		26-61	110,000	100,000	0	0	
		26-62	110,000	100,000	0	0	
		26-63	110,000	100,000	0	0	
		26-64	110,000	100,000	0	0	
		26-65	110,000	100,000	0	0	
		26-66	110,000	100,000	0	0	
		26-67	110,000	100,000	0	0	
		26-68	110,000	100,000	0	0	
		26-69	110,000	100,000	0	0	
		26-70	110,000	100,000	0	0	
		26-71	110,000	100,000	0	0	
		26-72	110,000	100,000	0	0	
		26-73	110,000	100,000	0	0	
		26-74	110,000	100,000	0	0	
		26-75	110,000	100,000	0	0	
		26-76	110,000	100,000	0	0	
		26-77	110,000	100,000	0	0	
		26-78	110,000	100,000	0	0	
		26-79	110,000	100,000	0	0	
		26-80	110,000	100,000	0	0	
		26-81	110,000	100,000	0	0	
		26-82	110,000	100,000	0	0	
		26-83	110,000	100,000	0	0	
		26-84	110,000	100,000	0	0	
		26-85	110,000	100,000	0	0	
		26-86	110,000	100,000	0	0	
		26-87	110,000	100,000	0	0	
		26-88	110,000	100,000	0	0	
		26-89	110,000	100,000	0	0	
		26-90	110,000	100,000	0	0	
		26-91	110,000	100,000	0	0	
		26-92	110,000	100,000	0	0	
		26-93	110,000	100,000	0	0	
		26-94	110,000	100,000	0	0	
		26-95	110,000	100,000	0	0	
		26-96	110,000	100,000	0	0	
		26-97	110,000	100,000	0	0	
		26-98	110,000	100,000	0	0	
		26-99	110,000	100,000	0	0	
		26-100	110,000	100,000	0	0	

From material balance.

**Assumption

***Tests have been conducted at several (other) locations with good agreement.

****Polyethylene fines may also be entrained in the air stream.

Note: For non-polluting streams, please see Simplified Flow Diagram Figure 1B-1, (having B-209) and Table IV.

TABLE I P-III
NATIONAL EMISSIONS INVENTORY
LOW DENSITY POLYETHYLENE PRODUCTION

[illegible]

*“Equipment volume plus purge procedure” used to determine composition and flow.

*Samples taken during the last revisions to the

*Flow determined from purge air system capacity.

*In addition, there are "compounding" and "fines removal" vents which total less than 2 lbs./hr. LIME fines

Note: For non-polluting streams, please see Simplified Flow Diagram Figure D-1, (covering p-209) and Table IV.

TABLE 1P-1111
NATIONAL EMISSIONS INVENTORY
LOW DENSITY POLYETHYLENE

Page 3 of 3

Company Location		24-11*** 150,000 150,000 0		24-12 150,000 150,000 0	
EPA Code No.		24-11***		24-12	
Capacity - Tons of LD Polyethylene/Yr.		150,000		150,000	
Average Production - Tons of LDPE/Yr.		150,000		150,000	
Seasonal Range in Production - % of Max.		0		0	
Emissions to Atmosphere		0		0	
Stream Letter on Flow Diagram		C		D	
Description		Other Emissions		Materials	
Flow - Lb./Hr. of Pollutants		211		Handling Vent****	
Flow Characteristic - Continuous or Intermittent		Continuous		Continuous	
If Intermittent - Hrs./Yr. Flow		0.0004		0.0004	
Composition - Ton/Ton LDPE		0.0003		0.0003	
Ethylene		None		None	
Polyethylene		0.0004		0.0004	
NOx		None		None	
Water Vapor		0.0004		0.0004	
Carbon Dioxide		0.0004		0.0004	
Hydrocarbons		None		None	
Sample Tap Location		None Indicated		None	
Date or Frequency of Sampling		None Indicated		None	
Type of Analysis		None Indicated		None	
Odor Problem		None Indicated		None	
Vent Stacks		None Indicated		None	
Flow SCPM per Stack		None Indicated		None	
Number		None Indicated		None	
Height - Feet		None Indicated		None	
Diameter - Inches		None Indicated		None	
Exit Gas Temperature - F		None Indicated		None	
Emission Control Devices		None Indicated		None	
Type - Flare		None Indicated		None	
Bag House		None Indicated		None	
Cyclone		None Indicated		None	
Water Scrubber		None Indicated		None	
Other		None Indicated		None	
Catalog I. D. No.		None Indicated		None	
Total Hydrocarbon Emissions - Ton/Ton LDPE		None Indicated		None	
Total Particulate - ton/ton LDPE		None Indicated		None	
Total NOx - Ton/Ton LDPE		None Indicated		None	
Total SOx - Ton/Ton LDPE		None Indicated		None	
Total CO - Ton/Ton LDPE		None Indicated		None	

*Composition calculated.

**Estimate based on plant-wide material balance.

***Combustion products from a liquids incinerator also exist, in addition to "other emissions". These combustion products present no emissions inventory contribution (the SOx and CO are so low that they have no significance as pollutants).

****Composition & flow estimated from material balance and estimated pneumatic conveyor blower capacity.

*****Composition based on process composition - flow estimated.

Note: For non-polluting streams, please see Simplified Flow Diagram Figure 1D-1 (Drawing R-209) and Table IV.

FLARE SYSTEM

Device I. D. Number
 Types of Compounds Flared
 Amount Flared - lb./hr.
 Device or Stack Height - Ft.
 Stack Diameter @ tip - inches
 Installed Cost - Mat'l. & Labor - \$
 Installed Cost - Mat'l. & Labor - \$ (1972)
 Operating Cost - Annual - \$ (1972)
 Operating Cost - Annual - \$/lb. of LDPE Production
 Efficiency - CCR - %
 Efficiency - SRR - %
 Years Installed
 Source

24-12 102
 Various Lt. H.C.
 Normally zero (5%)
 120
 36
 530,000

 16,000

 Presumed near 100%
 Presumed over 99.5%
 1961-1969
 John Zink tip
 Minneapolis Tank Stack

24-3 101
 Various Lt. H.C.
 14,000**
 115
 10
 83,000
 0.0377
 9,400
 0.0043
 Presumed near 100%
 Presumed over 99.5%
 1967-1970
 John Zink***

24-11 101
 Various Lt. H.C.
 1,000
 100
 20
 15,000
 0.0552
 3,500
 0.0012
 Presumed near 100%
 Presumed over 99.5%
 1940-1948
 In-house

MISCELLANEOUS

Device I. D. Number *
 Purpose - Control Emission, of
 Type

24-2 100
 LDPE Dust
 Cyclone,
 tangential, central pipe
 w/top outlet (no dimension indicated)
 1,810 SCFM/88 units
 (Total) 141,200
 0.0554
 5,100
 0.002
 Presumed near 100%
 1959-1965
 Nat'l. Conveyors Co. &
 Fuller Co.

24-5 101
 Various Lt. H.C.
 Collection, storage
 compression, and recycle
 to process
 Not indicated
 100,353
 0.0279
 (11,650 credit)
 (0.0032 credit)
 Not Indicated
 1955-1957
 In-house

24-11 102
 Combustible waste liquids
 Incinerator****
 w/25 HP air blower
 2,400 CFM
 200 CPH capacity
 97,000
 0.0323
 5,500
 0.0018
 Presumed Near 100%
 1949-1971
 Hauck, Mod. JRO-4125

24-12 101
 Combustible waste liquids
 Incinerator****
 w/pressurized liquid to firin
 run and steam atomization
 Capacity not indicated
 9,500
 0.0032
 1,000
 0.0003
 Presumed near 100%
 1971
 Nat'l. Alroil Burner Co.
 Size 35 single
 pedestal burner
 v/No. 3 SAR gun

TABLE 1P-12
 CATALOG OF EMISSION CONTROL DEVICES
 LOW DENSITY POLYETHYLENE

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.

**Design rate: ethylbenzene unit normally operates to keep this stream = zero

***Monitor system and streaming.

****These items are included as reported by the two respondents, 24-11 and 24-12; the resultant combustion products make no significant contribution as pollutants relative to the national emissions inventory.

*****Flare serves entire plant, no apportionment was made relative to LDPE plant emergencies.

Note: Respondents 24-6 and 24-7 indicate that there is no emission control device.

TABLE LP-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980*	Capacity 1980	Capacity to be Added by 1980	Economic Plant Size**	Number of New Units
5,269	564	4,705	19,000	21,100	16,395	400	41

186

Note: All capacities in MM LBS./YR.

*1980 demand based on Stanford Research Institute's
'Chemical Economics Handbook', Section 580.1330.

**Estimated.

TABLE LP-VI
EMISSION SOURCE SUMMARY*
TON/TON OF LDPE

Emissions	Source				Total
	Compressor Purge	Reactor	Materials Handling	Gas-Separation Recovery Operation, Fugitive Emissions**	Flare***
Hydrocarbons	0.001	↑	0.005	0.010	TR 0.016
Particulates			0.0003	None	None 0.0003
NO _x		Negligible	None	None	<.0001 <0.0001
SO _x		↓	None	None	None 0
CO		↓	None	None	None 0

*At the time that this report was written, there were seven questionnaires on hand, with EPA Code No's. 24-2, 24-3, 24-5, 24-6, 24-7, 24-11, 24-13. The entries in the above table are adjudged to represent a modern plant with adequate capture and non-release of emissions candidates, and efficient particulate (polyethylene fines) removal means.

**The expressions "fugitive emissions" and "other emissions" are currently used interchangeably. "Other emissions" is the label used in the questionnaire form, Section VIII.

***Flares, where used are either intermittent, or also served other plant processes.

TABLE LP-VII
WEIGHTED EMISSION RATES

Chemical Low Density Polyethylene
Process High Pressure Polymerization
New Added Capacity by 1980 16,395 MM Lbs./Yr.

Pollutant	Emissions, Lbs./Lb.	Increased Emissions MM Lbs./Year	Weighting Factors	Weighted Emissions MM Lbs./Year
Hydrocarbons	0.016	262	80	21,000
Particulates	0.0003	5	60	300
NO _x	Negligible	Negligible	40	
SO _x	None	0	20	
CO	None	0	1	

Significant Emission Index = 21,300 (MM Lbs./Year)

Appendix I, II, & III

APPENDIX I

FINAL ADDRESS LIST

Air Products & Chemicals, Inc.
P. O. Box 97
Calvert City, Kentucky

Attention: Mr. Howard Watson

Allied Chemical Corp.
Morristown, New Jersey

Attention: Mr. A. J. VonFrank
Director Air & Water
Pollution Control

American Chemical Corp.
2112 E. 223rd
Long Beach, California 90810

Attention: Mr. H. J. Kandel

American Cyanamid Company
Bound Brook, New Jersey

Attention: Mr. R. Phelps

American Enka Corporation
Enka, North Carolina 28728

Attention: Mr. Bennet

American Synthetic Rubber Corp.
Box 360
Louisville, Kentucky 40201

Attention: Mr. H. W. Cable

Amoco Chemicals Corporation
130 E. Randolph Drive
Chicago, Illinois

Attention: Mr. H. M. Brennan, Director
of Environmental Control Div.

Ashland Oil Inc.
1409 Winchester Ave.
Ashland, Kentucky 41101

Attention: Mr. O. J. Zandona

Borden Chemical Co.
50 W. Broad Street
Columbus, Ohio 43215

Attention: Mr. Henry Schmidt

Celanese Chemical Company
Box 9077
Corpus Christi, Texas 78408

Attention: Mr. R. H. Maurer

Chemplex Company
3100 Gulf Road
Rolling Meadows, Illinois 60008

Attention: Mr. P. Jarrat

Chevron Chemical Company
200 Bush Street
San Francisco, California 94104

Attention: Mr. W. G. Toland

Cities Service Inc.
70 Pine Street
New York City, NY 10005

Attention: Mr. C. P. Goforth

Clark Chemical Corporation
Blue Island Refinery
131 Kedzie Avenue
Blue Island, Illinois

Attention: Mr. R. Bruggink, Director
of Environmental Control

Columbia Nitrogen Corporation
Box 1483
Augusta, Georgia 30903

Attention: Mr. T. F. Champion

Continental Chemical Co.
Park 80 Plaza East
Saddlebrook, NJ 07662

Attention: Mr. J. D. Burns

Cosden Oil & Chemical Co.
Box 1311
Big Spring, Texas 79720

Attention: Mr. W. Gibson

Dart Industries, Inc.
P. O. Box 3157
Terminal Annex
Los Angeles, California 90051

Attention: Mr. R. M. Knight
Pres. Chemical Group

Diamond Plastics
P. O. Box 666
Paramount, California 70723

Attention: Mr. Ben Wadsworth

Diamond Shamrock Chem. Co.
International Division
Union Commerce Building
Cleveland, Ohio 44115

Attention: Mr. W. P. Taylor, Manager
Environ. Control Engineering

Dow Badische Company
Williamsburg, Virginia 23185

Attention: Mr. L. D. Hoblit

Dow Chemical Co. - USA
2020 Building
Abbott Road Center
Midland, Michigan 48640

Attention: Mr. C. E. Otis
Environmental Affairs Div.

E. I. DuPont de Nemours & Co.
Louviers Building
Wilmington, Delaware 19898

Attention: Mr. W. R. Chalker
Marketing Services Dept.

Eastman Chemicals Products, Inc.
Kingsport, Tennessee

Attention: Mr. J. A. Mitchell
Executive Vice President
Manufacturing

El Paso Products Company
Box 3986
Odessa, Texas 79760

Attention: Mr. N. Wright,
Utility and Pollution
Control Department

Enjay Chemical Company
1333 W. Loop South
Houston, Texas

Attention: Mr. T. H. Rhodes

Escambia Chemical Corporation
P. O. Box 467
Pensacola, Florida

Attention: Mr. A. K. McMillan

Ethyl Corporation
P. O. Box 341
Baton Rouge, Louisiana 70821

Attention: Mr. J. H. Huguet

Fibre Industries Inc.
P. O. Box 1749
Greenville, South Carolina 29602

Attention: Mr. Betts

Firestone Plastics Company
Box 699
Pottstown, Pennsylvania 19464

Attention: Mr. C. J. Kleinart

Firestone Synthetic Rubber Co.
381 W. Wilbeth Road
Akron, Ohio 44301

Attention: Mr. R. Pikna

Firestone Plastics Company
Hopewell, Virginia

Attention: Mr. J. Spohn

FMC - Allied Corporation
P. O. Box 8127
South Charleston, W. VA 25303

Attention: Mr. E. E. Sutton

FMC Corporation
1617 J.F.K. Boulevard
Philadelphia, PA

Attention: Mr. R. C. Tower

Foster Grant Co., Inc.
289 Main Street
Ledminster, Mass. 01453

Attention: Mr. W. Mason

G.A.F. Corporation
140 W. 51st Street
New York, NY 10020

Attention: Mr. T. A. Dent, V.P.
of Engineering

General Tire & Rubber Company
1 General Street
Akron, Ohio 44309

Attention: Mr. R. W. Laundrie

Georgia-Pacific Company
900 S.W. 5th Avenue
Portland, Oregon 97204

Attention: Mr. V. Tretter
Sr. Environmental Eng.

Getty Oil Company
Delaware City, Delaware 19706

Attention: Mr. Gordon G. Gaddis

B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, Ohio 44131

Attention: Mr. W. Bixby

Goodyear Tire & Rubber Co.
1144 E. Market Street
Akron, Ohio 44316

Attention: Mr. B. C. Johnson, Manager
Environmental Engineering

Great American Chemical Company
650 Water Street
Fitchburg, Mass.

Attention: Dr. Fuhrman

Gulf Oil Corporation
Box 1166
Pittsburgh, Pennsylvania

Attention: Mr. D. L. Matthews
Vice President -
Chemicals Department

Hercules Incorporated
910 Market Street
Wilmington, Delaware

Attention: Dr. R. E. Chaddock

Hooker Chemical Corporation
1515 Summer Street
Stamford, Conn. 06905

Attention: Mr. J. Wilkenfeld

Houston Chemical Company
Box 3785
Beaumont, Texas 77704

Attention: Mr. J. J. McGovern

Hyston Fibers Division
American Hoechst Corporation
P. O. Box 5887
Spartensburg, SC 29301

Attention: Dr. Foerster

Jefferson Chemical Company
Box 53300
Houston, Texas 77052

Attention: Mr. M. A. Herring

Koch Chemical Company
N. Esperson Building
Houston, Texas 77002

Attention: Mr. R. E. Lee

Koppers Company
1528 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. D. L. Einon

Marbon Division
Borg-Warner Corporation
Carville, Louisiana 70721

Attention: Mr. J. M. Black

Mobay Chemical Corporation
Parkway West & Rte 22-30
Pittsburgh, Pennsylvania 15205

Attention: Mr. Gene Powers

Mobil Chemical Company
150 E. 42nd Street
New York, NY 10017

Attention: Mr. W. J. Rosenbloom

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Attention: Mr. J. Depp, Director of
Corp. Engineering

National Distillers & Chem. Corp.
U.S. Industrial Chem. Co. Div.
99 Park Avenue
New York, NY 10016

Attention: Mr. J. G. Couch

National Starch & Chem. Co.
1700 W. Front Street
Plainfield, New Jersey 07063

Attention: Mr. Schlass

Northern Petrochemical Company
2350 E. Devon Avenue
Des Plaines, Illinois 60018

Attention: Mr. N. Wacks

Novamont Corporation
Neal Works
P. O. Box 189
Kenova, W. Virginia 25530

Attention: Mr. Fletcher

Olin Corporation
120 Long Ridge Road
Stamford, Conn.

Attention: Mr. C. L. Knowles

Pantasote Corporation
26 Jefferson Street
Passaic, New Jersey

Attention: Mr. R. Vath

Pennwalt Corporation
Pennwalt Building
3 Parkway
Philadelphia, PA 19102

Attention: Mr. J. McWhirter

Petro-Tex Chemical Corporation
Box 2584
Houston, Texas 77001

Attention: Mr. R. Pruessner

Phillips Petroleum Co.
10 - Phillips Bldg.
Bartlesville, Oklahoma 74004

Attention: Mr. B. F. Ballard

Polymer Corporation, Ltd.
S. Vidal Street
Sarnia, Ontario
Canada

Attention: Mr. J. H. Langstaff
General Manager
Latex Division

Polyvinyl Chemicals Inc.
730 Main Street
Wilmington, Mass. 01887

Attention: Mr. S. Feldman, Director of
Manufacturing - Engineering

PPG Industries Inc.
One-Gateway Center
Pittsburgh, Pennsylvania 15222

Attention: Mr. Z. G. Bell

Reichold Chemicals Inc.
601-707 Woodward Hts. Bldg.
Detroit, Michigan 48220

Attention: Mr. S. Hewett

Rohm & Haas
Independence Mall West
Philadelphia, PA 19105

Attention: Mr. D. W. Kenny

Shell Chemical Co.
2525 Muirworth Drive
Houston, Texas 77025

Attention: Dr. R.L. Maycock
Environ. Eng. Div.

Sinclair-Koppers Chem. Co.
901 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. R. C. Smith

Skelly Oil Company
Box 1121
El Dorado, Kansas 67042

Attention: Mr. R. B. Miller

Standard Brands Chem. Industries
Drawer K
Dover, Delaware 19901

Attention: Mr. E. Gienger, Pres.

Stauffer Chemical Co.
Westport, Connecticut

Attention: Mr. E. L. Conant

Stepan Chemical Company
Edens & Winnetka Road
Northfield, Illinois 60093

Attention: Mr. F. Q. Stepan
V.P. - Industrial Chemicals

Tenneco Chemicals Inc.
Park 80 Plaza - West 1
Saddlebrook, NJ 07662

Attention: Mr. W. P. Anderson

Texas - U.S. Chemical Company
Box 667
Port Neches, Texas 77651

Attention: Mr. H. R. Norsworth

Thompson Plastics
Assonet, Mass. 02702

Attention: Mr. S. Cupach

Union Carbide Corporation
Box 8361
South Charleston, W. Virginia 25303

Attention: Mr. G. J. Hanks, Manager
Environ. Protection
Chem. & Plastics Division

Uniroyal Incorporated
Oxford Management &
Research Center
Middlebury, Conn. 06749

Attention: Mr. F. N. Taff

The Upjohn Company
P. O. Box 685
La Porte, Texas

Attention: Mr. E. D. Ike

USS Chemicals Division
U.S. Steel Corporation
Pittsburgh, Pennsylvania 15230

Attention: Mr. Gradon Willard

W. R. Grace & Company
3 Hanover Square New York, NY 10004

Attention: Mr. Robt. Goodall

Wright Chemical Corporation
Acme Station
Briegelwood, North Carolina 28456

Attention: Mr. R. B. Catlett

Wyandotte Chemical Corp.
Wyandotte, Michigan 48192

Attention: Mr. John R. Hunter

Vulcan Materials Company
Chemicals Division
P.O. Box 545
Wichita, Kansas 67201

Attention: H.M. Campbell
Vice-President, Production

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs
Research Triangle Park, North Carolina 27711

Dear Sir:

The Environmental Protection Agency, Office of Air Programs is engaged in a study of atmospheric emissions from the Petrochemical Industry. The primary purpose of this study is to gather information that will be used to develop New Stationary Source Performance Standards which are defined in Section 111 of the Clean Air Act as amended December 31, 1970 (Public Law 91604). These new source standards will not be set as part of this study but will be based (to a large extent) on the data collected during this study.

A substantial part of the work required for this study will be performed under contract by the Houdry Division of Air Products and Chemicals. Several other companies not yet chosen will assist in the source sampling phase of the work.

Very little has been published on atmospheric emissions from the petrochemical industry. The first part of this study will therefore rank the most important petrochemical processes in their order of importance in regard to atmospheric emissions. The Petrochemical Emissions Survey Questionnaire will be the primary source of data during the first phase. This ranking will be based on the amount and type of emissions from the process, the number of similar processes and the expected growth of the process. A second in-depth phase of the study to document emissions more completely will be based on information obtained through actual stack sampling.

Attached you will find a copy of the petrochemical questionnaire which you are requested to complete and return to the Environmental Protection Agency within forty-two (42) calendar days.

You are required by Section 114 of the Clean Air Act to complete each applicable part of this questionnaire except for question II.4. and II.5. These two questions are concerned with the water and solid waste generated by the process itself not with that generated by the emission control equipment. This information would be of a value to the EPA and your answers will be appreciated.

This questionnaire is to be completed using the information presently available to your company. We are not asking that you perform special non-routine measurements of emissions streams. We are asking for results of measurements that you have made or for estimates when measurements have not been made. Where requested information is not available, please mark sections "not available". Where the requested information is not applicable to the subject process, mark the questionnaire sections "not applicable". A sample questionnaire, filled out for a fictitious process is enclosed for your guidance.

It is the opinion of this office that for most processes it should be possible to answer all survey questions without revealing any confidential information or trade secrets. However, if you believe that any of the information that we request would reveal a trade secret if divulged you should clearly identify such information on the completed questionnaire. Submit, with the completed questionnaire, a written justification explaining the reason for confidential status for each item including any supportive data or legal authority. Forward a duplicate of your claim and supporting material, without the questionnaire data, to our counsel, Mr. Robert Baum, Assistant General Counsel, Air Quality and Radiation Division, Environmental Protection Agency, Room 17B41, 5600 Fishers Lane, Rockville, Maryland 20852. Emission data cannot be considered confidential.

Final authority for determining the status of the information resides with the Environmental Protection Agency. A reply describing the decision reached will be made as soon as possible after receipt of the claim and supporting information. During the period before the final determination this office will honor any request to treat the questionnaire information as confidential.

Information declared to be a trade secret is subject to protection from being published, divulged, disclosed or made known in any manner or to any extent by Section 1905 of Title 18 of the United States Code. The disclosure of such information, except as authorized by law, shall result in a fine of not more than \$1,000 or imprisonment of not more than one year, or both; and shall result in removal of the individual from his office or employment.

Although it should be noted that Section 114, Subsection C of the Clean Air Act allows such information to be disclosed "to other officers, employees, or authorized representatives of the United States concerned with carrying out the Act or when relevant in any proceeding under this Act," no confidential information will be revealed to any private concern employed by the Environmental Protection Agency to assist in this study.

The handling and storage of information for which the determination is pending or information which has been determined to be of a confidential nature is carefully controlled. Preliminary control procedures require that the material be labeled confidential and stored in a locked file.

The complete form should be mailed to:

Mr. Leslie B. Evans
Environmental Protection Agency
Office of Air Programs
Applied Technology Division
Research Triangle Park, NC 27711

It is possible that additional copies of this questionnaire which will request information covering other petrochemical processes or other plants using the same process and operated by your organization will be sent to you in the course of this study. Clarification of items contained in the questionnaire may be obtained from Mr. Evans by telephone at 919/688-8146. Thank you for your help in this matter.

Sincerely,

Leslie B. Evans

Leslie B. Evans
Industrial Studies Branch

Petrochemical Questionnaire

Instructions

I. Capacity. Describe capacity of process by providing the following:

1. Process capacity. Give capacity in units per year and units per hour. An "actual" capacity is preferred but "published" or "name plate" capacity will be satisfactory if such capacity is reasonably correct. Do not give production.
2. Seasonal variation. Describe any significant seasonal variations in production.

As example an ammonia plant might produce more during spring and winter quarters:

quarter	Jan-Mar	April-June	July-Sept	Oct-Dec	Year Total
%	40	20	10	30	100%

II. Process. Describe the process used to manufacture the subject chemical by providing the following:

1. Process name. If the process has a common name or description, give this. If any portion of the process (e.g., product recovery method) has a common name, give this.
2. Block Diagram. Provide a block diagram of the process showing the major process steps and stream flows.
 - (a) Show on block diagram all streams described below. Identify each required stream by letter. (A,B,C, etc.) In general the streams that must be identified are (1) the gaseous emissions streams before and after any control device and (2) the gaseous or liquid streams which, after leaving the process site, produce gaseous emissions during further processing or combustion.
 - (i) Any gaseous waste streams before and after any pollution device should be shown and identified.
 - (ii) Streams from rupture disks or pressure relief valves which protect equipment from operating upsets but discharges less than once every year need not be shown.
 - (iii) Emissions from pressure relief systems that normally discharge during power failures or other emergencies should be shown, identified by letter and labeled "emergency".

- (iv) Emissions from fueled heaters such as "heat transfer medium" heaters, steam generators, or cracking furnaces need not be shown if they are fueled completely by fuels listed in Question VII and are not used to incinerate by-products or off gases.
 - (v) Emissions from Claus units associated with process need not be shown. Stream to Claus unit should be shown and identified with letter.
 - (vi) Emissions from a central power plant (or steam plant) which burns a liquid fuel produced as a by-product of this process need not be shown. Such liquid fuel should be shown and identified by letter.
 - (vii) Emissions from a central power plant (or steam plant) which burns a gaseous fuel produced as a by-product of this process need not be shown. Such gaseous fuel should be shown and identified by letter.
- (b) Show all gaseous emission control devices. Identify each control device on the block diagram by a three digit number (101, 102, 103, etc.)
 - (c) Show all stacks or vents that vent streams listed in (a) and (b) above. If a stack or vent discharges emissions from more than one source, label this stack or vent with a letter in sequence started in II.2.a. (D,E,F, etc.) If a stack or vent discharges emissions from only one source label the stack with the same letter as the emission stream.
3. Raw material and product. Give approximate chemical composition and approximate amount (on yearly basis and at capacity given in I.1) of all raw-materials, products and by-products. If composition or amounts vary, give ranges. Composition may be given in commonly accepted terms when a chemical analysis would be inappropriate. The description "light straight-run naphtha" would be adequate.
 4. Waste water. Is there a waste water discharge from this process which is (eventually) discharged to a receiving body of water? Is this waste water treated by you or by others? Give the approximate volume and indicate whether this is measured or estimated.

5. Waste solids. Is there a waste solids discharge from this process? How is it disposed of? Give the approximate daily total of waste solids and indicate if this is measured or estimated.

III. Emissions (composition and flow): For each stream requested in II.2.a. and shown on the block diagram by letter provide the following: (Use separate sheets for each identified location - 6 copies are provided). All of the questions will not be applicable for each stream.

As an example, question 10, odor problem, applies only to streams which are emitted to the atmosphere.

1. Chemical composition and flow. Give composition as completely as possible from information you have available. Do not omit trace constituents if they are known. If anything (e.g. fuel) is added upstream of any emission control devices, give the chemical composition and flow prior to the addition, and give the quantity and composition of the added material. If liquids or solids are present (in gas stream) provide the composition and amount of these also. Give flow volume (SCFM), temperature (F°) and pressure (psig or inches H_2O).
2. Variation in chemical composition and flow. If average stream composition or flow varies significantly over some period of time during normal or abnormal operation, discuss this variation and its frequency. Relate this to the average and range of composition given in III.1.

As examples:

"During start-up (once a month) the benzene is about 12% by volume for one hour" or "the benzene can be expected to go from 5% to 9% by volume during life of catalyst, the 'average' figure given is about average over the catalyst life" or "power failures occur about once each winter causing stream A to increase from 0 to (initially) 50,000 lbs/hr., and about 8,000 lbs is vented over a 15 minute period."

3. Production rate during sampling. If stream composition and volume flow rates given in answer to questions III.1. and III.2. were measured at a plant production rate different than the capacity of the plant given in I.1. give the rate at which the measurements were made.

As example:

Figures given for this stream (A) were made when plant was operating at 90% of capacity given in I.1.

4. Methods used to determine composition and flow. Is information from material balance, from sample and analysis, or other? Describe briefly.
5. Sampling procedure. If samples have been taken, give summary description of sampling procedure or give reference if described in open literature.
6. Analytical procedure. If samples have been taken, give summary description of analytical procedure or give reference if described in open literature.
7. Sampling frequency. How often is the stream sampled?

As Examples:

"continuous monitor" or "twice a shift for last 18 months" or "once in the fall of 1943".

8. Confidence level. Give some idea how confident you are in regard to compositions in III.1.

As examples:

"probably correct $\pm 20\%$ " or "slightly better than wild guess".

9. Ease of sampling. How difficult is it to sample this stream?

As examples:

"sample line runs into control room" or "sample port provided but accessible only with 20-ft. ladder."

10. Odor problem. Is the odor of this emission detectable at ground level on the plant property or off the plant property? If odors carry beyond the plant property are they detectable frequently or infrequently? Have you received a community odor complaint traceable to this source in the past year? Has the odorous material been chemically identified? What is it?

IV. Emission control device. Supply the following information for each control device shown on the block diagram. (Use separate sheets for each - 3 copies are provided).

1. Engineering description. Give brief description and process sketch of the control device. Attach print or other description if you prefer. Show utilities used, steam produced, product recovered, etc. Give manufacturer, model number and size (if applicable). Give complete (applicable) operating conditions, i.e. flows, temperatures, pressure drops, etc.
2. Capital cost of emission control system.
 - (a) Give capital cost for the emission control device as it is described in IV.1. above; i.e., if equipment has been modified or rebuilt give your best estimate of capital cost of equipment now in service. For the total installed cost give the approximate breakdown by year in which cost was incurred.

As example:

Major equipment cost	\$155,000
Total installed cost	<u>\$250,000</u>
Year	Cost
1963	\$160,000
1964	40,000
1971	<u>50,000</u>
	\$250,000

- (b) On the check list given mark whether the items listed are included in total cost as given above. Give one sentence explanation when required but do not give dollar amounts.
 - (c) Was outside engineering contractor used and was cost included in capital cost?
 - (d) Was in-house engineering used and was cost included in capital cost?
 - (e) Was emission control equipment installed when plant was built?
3. Operating cost of emission control system. Give the best estimate of cost of operating emission control system in dollars per year with process operated at capacity given in I.1. Other disposal (g) would include, as example, the cost of incinerating a by-product stream which has no value.

- V. Stack or vent description. Each stack or vent should have been identified by letter on the block diagram. Provide the requested information for each stack. Stack flow, V.4. should be entered only when it is not possible to calculate this number by adding gas flows given in III.1.

An example would be when an off gas from the process is discharged into a power plant stack.

- VI. Tankage. Give information requested for all tankage larger than 20,000 gallons associated with the process and normally held at atmospheric pressure (include raw material, process, product and by-product tankage). Method of vapor conservation (3.) might include, as examples:

"none, tank vents to air"

"floating roof"

"vapor recovery by compression and absorption".

- VII. Fuels. If fuels are used in the process give the amount used on a yearly basis at capacity given in I.1. Do not include fuel used in steam power plants. Give sulfur content. Identify each fuel as to its source (natural gas pipeline, process waste stream, Pennsylvania soft coal). Is the fuel used only as a heat source (as with in-line burner)?

- VIII. Other emissions. If there is a loss of a volatile material from the plants through system leaks, valve stems, safety valves, pump seals, line blowing, etc., this loss is an emission. In a large complex high pressure process this loss may be several percent of the product. Has this loss been determined by material balance or other method? What is it? Give best estimate.

- IX. Future plans. Describe, in a paragraph, your program for the future installation of air pollution control equipment for this unit or for future improvements in the process which will reduce emissions.

This example questionnaire has been
completed for a fictitious company
and process.

Example
Questionnaire

Air Pollution Control Engineering and Cost Study of the Petrochemical Industry

Please read instructions before completing questionnaire.

Subject chemical: Pyrrole

Principal by-products: Pyrrolidone

Parent corporation name: Orivne Petrochemical Co.

Subsidiary name: Noissime Division

Mailing address: P.O. Box 1234

Rianaelc, North Carolina, 27700

Plant name: Rianaelc Plant

Physical location: 30 miles N.W. Durham, North Carolina

(include county and
air quality control
region) Orange County; Eastern Piedmont Intrastate (Region IV)

Person EPA should contact regarding information supplied in this questionnaire

Name: John Doe

Title: Supervisor of Process Development

Mailing address: Noissime Division of O.P.C.

P.O. Box 1234

Rianaelc, North Carolina, 27700

Telephone number: 919 XXX XXXX

Date questionnaire completed: May 30, 1972

I. Capacity.

1. Process capacity. (not production)

80,000,000 lbs. per year

10,000 lbs. per hour

2. Seasonal variation. (of production)

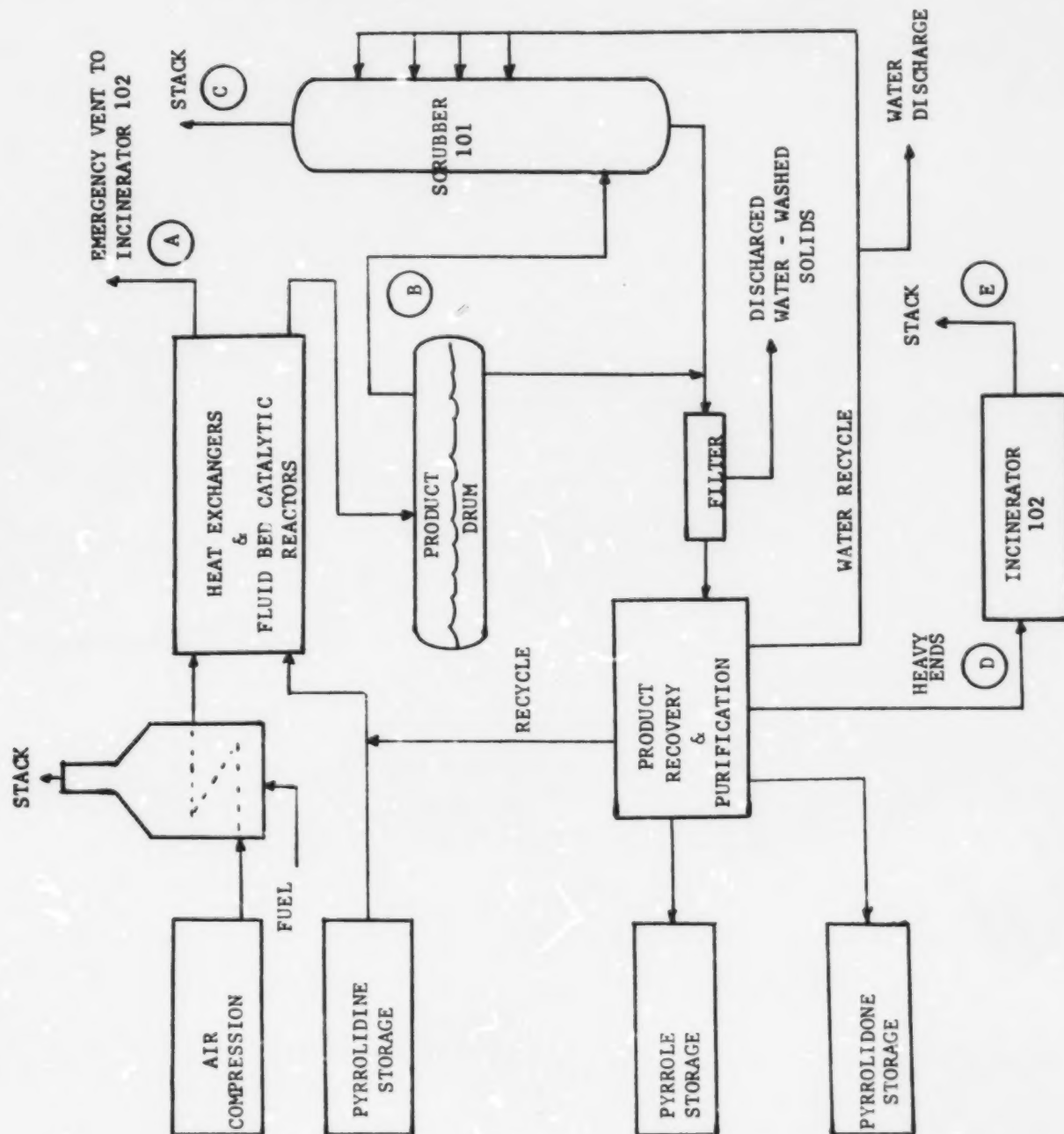
quarter	1	2	3	4	year total
%	<u>30</u>	<u>20</u>	<u>20</u>	<u>30</u>	<u>100%</u>

II. Process.

1. Process name.

Reivrep - Process (oxidative dehydrogenation of pyrrolidine)

2. Block diagram.



II. Process. (Continued)

3. Raw materials and products

Raw materials

<u>Name</u>	<u>Quantity</u>	<u>Composition</u>
<u>Pyrrolidine</u>	<u>130,000,000 lbs/yr.</u>	<u>pyrrolidine</u> 98%
		<u>other amines</u> 2%

Product and by-products

<u>Name</u>	<u>Quantity</u>	<u>Composition</u>
<u>Pyrrole</u>	<u>80,000,000 lbs/yr.</u>	<u>pyrrole</u> 99.5%
<u>Pyrrolidone</u>	<u>20,000,000 lbs/yr.</u>	<u>pyrrolidone</u> 99.5%

II. Process. (Continued)

4. Waste water.

750 gal/hr. treated by us, measured in treatment unit.

5. Waste solids.

200 lbs/hr. catalyst dust from filter. Estimated average quantity hauled away by solids waste disposal contractor.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter A.

1. Flow ? Temperature ? Pressure ?

Component Name	Formula	State	Average amount or composition	Composition Range
-------------------	---------	-------	----------------------------------	----------------------

Particulate	*	Solid		
-------------	---	-------	--	--

Depending upon cause of emergency, emissions could range from contaminated feed to contaminated product.

Upset durations seldom exceed 15 minutes during which time incinerator operation would be modified. For initial 1-2 minutes after upset pollutants might leave incinerator stack. Following that, stack gases will be nearly 100% CO₂, H₂O & N₂. On average, such upsets occur two or three times per year. Particulates are possible, depending upon cause of upset. One such upset occurred in 1969.

* Particulate matter should be described as fully as possible.

III. Continued For stream flow shown on block diagram by letter A.

2. Composition variation.

See III-1

3. Production rate during sampling.

Never Sampled

4. Method used to determine composition and flow.

Not applicable

III. Continued For stream flow shown on block diagram by letter A.

5. Sampling procedure.

Not Applicable

6. Analytical procedure.

Not Applicable

7. Sampling frequency.

Never

III. Continued For stream flow shown on block diagram by letter A.

8. Confidence level.

Not Applicable

9. Ease of sampling.

Impossible

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level
on the plant property? Yes/no Off the plant property? Yes/no
If odors carry beyond the plant property are they detectable
infrequently? Yes/no Frequently? Yes/no Have you received a
community odor complaint traceable to this source in the past
year? Yes/no Has the odorous material been chemically identified?
Yes/no What is it? _____

Not Applicable

Six copies provided
this section

III.1. Emissions (composition and flow).

Stream flow shown on block diagram by letter B.

1. Flow 10,000 SCFH Temperature 110°F Pressure 25 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	150 lbs./hour	100-200 lbs./hour
Nitrogen	N ₂	Gas	83.8 Vol. %	80-85%
Oxygen	O ₂	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO ₂	Gas	1.4 "	1-2%
Hydrogen	H ₂	Gas	2.1 "	2-2.5%
Water	H ₂ O	Vapor	7.1 "	6.5-7.5%
Various Amines	**	Vapor	0.1 "	0.05-0.2%
Nitrogen Oxides	NO _x	Gas	300 VPPM	200-500 VPPM

* Particulate matter should be described as fully as possible. Catalyst Dust (composition is proprietary) contains cobalt and chromium on alumina base. 100% less than 15 microns; 60% less than 10 microns; 20% less than 5 microns; 5% less than 1 micron.

** Composition unknown - mixture of feed, products and other amines.

III. Continued For stream flow shown on block diagram by letter B.

2. Composition variation.

During 2nd and 3rd quarter when plant is operated below capacity, nitrogen is at high end of range and all other materials near low end. During start-up or plant upset (average about 50 hours/year) nitrogen is near low end of range and all other materials near high end.

3. Production rate during sampling.

Average composition based on rated capacity.

4. Method used to determine composition and flow.

Engineering calculation and plant material balance (flow).

Composition calculated on basis of stream "C" analysis and estimated amine losses prior to installation of scrubber.

III. Continued For stream flow shown on block diagram by letter B.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never Analyzed.

7. Sampling frequency.

See (5) above.

III. Continued For stream flow shown on block diagram by letter B.

8. Confidence level.

+10%

9. Ease of sampling.

No sample taps are available, but one could be easily installed in readily accessible location. However, it would not be 8 pipe diameters from a disturbance.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no

If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a

community odor complaint traceable to this source in the past

year? Yes/no Has the odorous material been chemically identified?

Yes/no What is it? _____

No applicable - this stream is no longer emitted to the atmosphere.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter C.

1. Flow 10,000SCFM Temperature 100°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	10 lbs./hour	5-20 lbs./hour
Nitrogen	N ₂	Gas	83.9 Vol. %	80-85%
Oxygen	O ₂	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO ₂	Gas	1.4 "	1-2%
Hydrogen	H ₂	Gas	2.1 "	2-2.5%
Water	H ₂ O	Vapor	7.1 "	6.5-7.5%
Various Amine	**	Vapor	50 YPPMV	30-100 PPMV
Nitrogen Oxides	NO _x	Gas	300 YPPMV	200-500 PPMV

* Particulate matter should be described as fully as possible. See "B". Size distribution 100% less than 5 microns; 60% less than 1 micron.

** See "B".

III. Continued For stream flow shown on block diagram by letter C.

2. Composition variation.

See "B"

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

See "B" for flow. Specific analysis methods are given in III-6(C)

III. Continued For stream flow shown on block diagram by letter C.

5. Sampling procedure.

- a. Particulates and moisture collected in sampling train as detailed in Federal Register, Dec. 23, 1971 (Method 5).
- b. NO_x sampled by EPA Method 7.
- c. Other constituents collected using grab sampling procedures for collection of gas. Sample size 10 liters in stainless steel tank.

6. Analytical procedure.

- a. Particulates and moisture determined gravimetrically as detailed in Federal Register, Dec. 23, 1971. (Method 5)
- b. NO_x determined by EPA method 7.
- c. Hydrogen, oxygen, and nitrogen determined by mass spectrometer analysis at local university.

Amine, CO and CO_2 determined by infra-red analysis.

7. Sampling frequency.

Once, - one month after scrubber was put on stream.

III. Continued For stream flow shown on block diagram by letter C.

8. Confidence level.

Oxygen, CO₂, CO and H may be $\pm 10\%$.

Nitrogen would be better than this, perhaps $\pm 5\%$

Amines are near limit of detection - $\pm 50\%$.

9. Ease of sampling.

Difficult - only sample tap is six feet above top of scrubber tower - approximately 65 feet in air - reached by caged ladders.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no

If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it? Amine compounds.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter D.

1. Flow 300 GPH Temperature 300°F Pressure 10 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Heavy Amines	$(CH_x)_yNH_z$	Liquid	100%	

* Particulate matter should be described as fully as possible. Very fine catalyst dust - never sampled
or analyzed - estimated to be 1-5 lbs./hour.

III. Continued For stream flow shown on block diagram by letter D.

2. Composition variation.

Not applicable - unknown - never analyzed.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Rotameter in liquid line for flow. Composition unknown.

III. Continued For stream flow shown on block diagram by letter D.

5. Sampling procedure.

Not applicable.

6. Analytical procedure.

Not applicable.

7. Sampling frequency.

Not applicable.

III. Continued For stream flow shown on block diagram by letter D.

8. Confidence level.

Not applicable.

9. Ease of sampling.

Liquid drain line is available at ground level. Could be used for sample tap.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no

If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it? _____

Not applicable - not an emitted stream.

Six copies provided
this section

III. 1 Emissions (composition and flow).

Stream flow shown on block diagram by letter E.

1. Flow 10,000SCFM Temperature 450°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Nitrogen	N ₂	Gas	77.0 Vol. %	76.5-77.5%
Oxygen	O ₂	Gas	9.2 Vol. %	9-9.5%
Carbon Dioxide	CO ₂	Gas	6.4 Vol. %	6-7%
Water	H ₂ O	Vapor	7.4 Vol. %	7-8%
Nitrogen Oxides	NO _x	Gas	150 VPPM	100-300 VPPM

* Particulate matter should be described as fully as possible. See "D"

III. Continued For stream flow shown on block diagram by letter E.

2. Composition variation.

Random variation depending on many variables such as production rate, ambient air temperature and humidity, catalyst age, etc., all within limits shown.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Calculation based on incinerator vendor's specifications, guarantees and laboratory tests.

III. Continued For stream flow shown on block diagram by letter E.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never analyzed

7. Sampling frequency.

See (5) above

III. Continued For stream flow shown on block diagram by letter E.

8. Confidence level.

+ 10%

9. Ease of sampling.

No sample tap, very hot stream, no access ladders, minimal insulation.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level
on the plant property? Yes/no Off the plant property? Yes/no

If odors carry beyond the plant property are they detectable
infrequently?* Yes/no Frequently? Yes/no Have you received a

community odor complaint traceable to this source in the past

year? Yes/no Has the odorous material been chemically identified?

Yes/no What is it? Amines

* Only during start-up or upset of the incinerator and then only

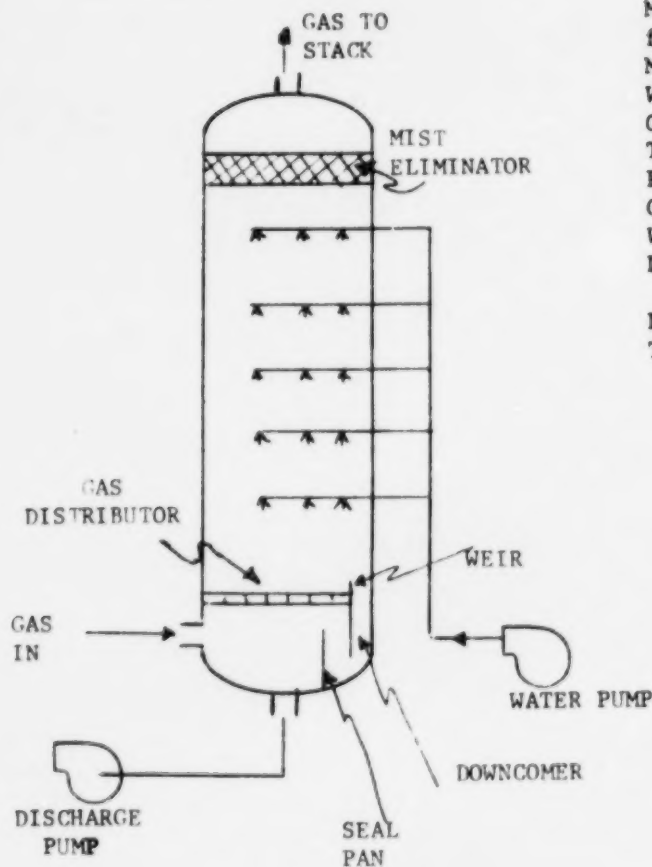
if atmospheric conditions are favorable for ground level detection.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 101.

1. Engineering description.



Multi-nozzle spray tower manu-
factured by Rebburcs Corp.
Model No. 10,000-W
Water rate: 100 GPM
Gas rate: 10,000 SCFM
Temperature: 100°F.
Pressure: Atmospheric
Gas AP: 8 in. H₂O
Water Pump Head: 150 Ft.
Discharge Pump Head: 100 Ft.

Diameter of Tower: 6 Ft.
T-T Length: 60 Ft.

Utilities:

35 HP for Pumps

10,000,000 BTU/Hr. Additional steam in product recovery section.

1500 GPM Additional cooling water circulation in product recovery section.

IV. Continued For device shown on block diagram by number 101.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost \$ 160,000

Total installed cost \$ 350,000

Year	Cost
<u>1968</u>	<u>\$350,000</u>
<u> </u>	<u> </u>
<u> </u>	<u> </u>

IV. Continued For device shown on block diagram by number 101.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Additional foundation required for scrubber.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Pigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
	X	Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 101.

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
X		Was in-house engineering used?
	X	Was cost included in capital cost?
	X	Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a) Utilities	\$ 68,000
(b) Chemicals *	10,000
(c) Labor (No Additional Operators)	-
(d) Maintenance (labor & materials)	14,000
(e) Water treatment (cost of treating any waste water produced by this control system) **	-
(f) Solids removal (cost of removing any waste solids produced by this control system)	20,000
(g) Other disposal	-
(h) By-product or product recovery CREDIT	\$89,000)
Total operating costs	\$ 23,000

* Additional cooling water treatment included in utility costs - this cost is for corrosion inhibition in scrubber.

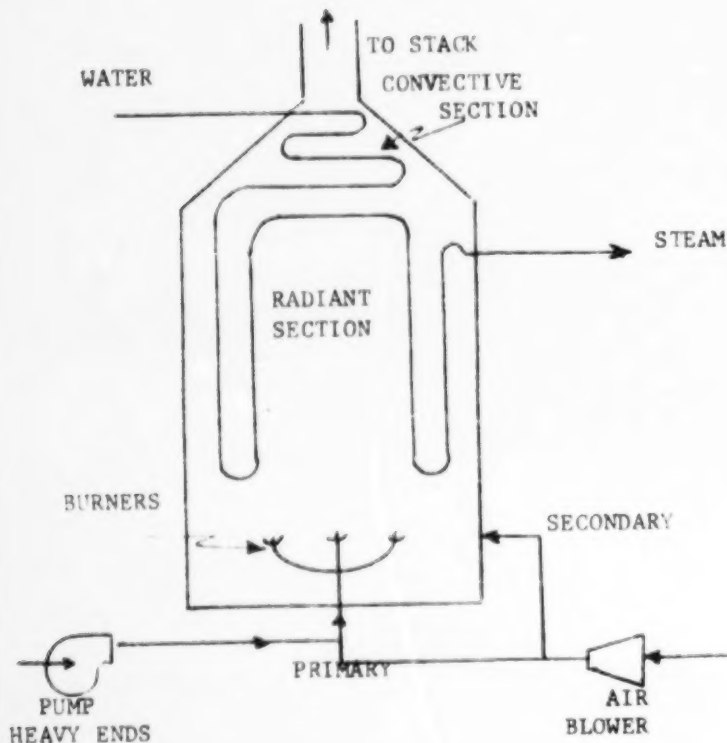
** Water waste is produced by process. It is treated at cost of \$30,000/year. This treatment was required before scrubber was installed.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 102.

1. Engineering description.



Steam Generator/Waste Incinerator

Manufactured by: Xoberif Corp.
Model No.: 40-H
Heavy Ends Rate: 300 GPH
Air Rate: 9,500 SCFM
Steam Rate: 20,000 lbs./hour
Vessel Diameter: 15 Ft.
Height: 40 Ft.
Tube Diameter: 3 in. nominal
Tube Length: (Material)
Convective (mild steel): 6,000 Ft.
Radiant (304 stainless): 2,000 Ft.

Utilities:

Heavy Ends Pump: 20 HP

Blower: 100 HP

IV. Continued For device shown on block diagram by number 102.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost \$ 350,000

Total installed cost \$ 1,000,000

Year	Cost
<u>1960</u>	<u>\$1,000,000</u>
<u> </u>	<u> </u>
<u> </u>	<u> </u>

IV. Continued For device shown on block diagram by number 102.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Cost prorated from total plant site costs.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
X		Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres, drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 102.

Yes	No	
<u>X</u>		Was outside engineering contractor used?
<u>X</u>		Was cost included in capital cost?
	<u>X</u>	Was in-house engineering used?
<u>X</u>		Was cost included in capital cost?
<u>X</u>		Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a) Utilities	\$ <u>5,000</u>
(b) Chemicals	<u>-</u>
(c) Labor ($\frac{1}{2}$ man per shift - excludes supervision & overhead)	<u>7,000</u>
(d) Maintenance (labor & materials)	<u>40,000</u>
(e) Water treatment (cost of treating any waste water produced by this control system)	<u>-</u>
(f) Solids removal (cost of removing any waste solids produced by this control system)	<u>-</u>
(g) Other disposal	<u>-</u>
(h) By-product or product recovery CREDIT- STEAM	<u>\$100,000</u>
Total operating credit	<u>\$ 48,000</u>

V. Stack or vent description.

For stack or vent shown on block diagram by letter C.

1. Stack height	<u>100 ft</u>
2. Stack diameter	<u>2 ft</u>
3. Gas temperature stack exit	<u>100 °F</u>
4. Stack flow *	<u>SCFM(70°F & 1 Atm.)</u>

For stack or vent shown on block diagram by letter E.

1. Stack height	<u>60 Ft.</u>
2. Stack diameter	<u>3 Ft.</u>
3. Gas temperature stack exit	<u>450°F</u>
4. Stack flow *	<u></u>

For stack or vent shown on block diagram by letter .

1. Stack height	<u></u>
2. Stack diameter	<u></u>
3. Gas temperature stack exit	<u></u>
4. Stack flow *	<u></u>

For stack or vent shown on block diagram by letter .

1. Stack height	<u></u>
2. Stack diameter	<u></u>
3. Gas temperature stack exit	<u></u>
4. Stack flow *	<u></u>

* See instructions

VI. Tankage.

No. of tanks	composition	temp.	capacity (each)	approximate turnovers per year	method of vapor conservation
3	Pyrrolidine (CH ₂) ₄ NH	Ambient	100,000 gal.(ea)	50	None, vents to air
4	Pyrrole (CH) ₄ NH	Ambient	100,000 gal.(ea)	25	"
1	Pyrrolidone (CH) ₂ CH ₂ CONH	Ambient	100,000 gal.(ea)	25	"

VII. Fuels.

800,000 gal./year fuel oil for fired air heater 3% sulfur.

VIII., Other emissions.

No other known emissions although minor leakages probably occur.

Engineering estimate of average losses is 0.01% of throughput or 13,000 lbs./year of amines.

IX. Future plans.

1. Current research on heavy amine stream indicates further processing will produce a marketable product - if so, incinerator will be shut down.
2. We are currently negotiating a long term contract to purchase 1% sulfur fuel oil from the Flused Oil Company.

APPENDIX III

FINAL QUESTIONNAIRE SUMMARY

<u>Chemical</u>	<u>Number of Questionnaires used as Basis for Report</u>
Acetaldehyde via Ethylene	1
via Ethanol	1
Acetic Acid via Methanol	2
via Putane	1
via Acetaldehyde	1
Acetic Anhydride	2
Acrylonitrile	4
Adipic Acid	4
Adiponitrile via Butadiene	1
via Adipic Acid	2
Carbon Black	7
Carbon Disulfide	4
Cyclohexanone	7
Dimethyl Terephthalate (+TPA)	6
Ethylene	13
Ethylene Dichloride via Oxychlorination	10
via Direct Chlorination	3
Ethylene Oxide	7
Formaldehyde via Silver Catalyst	12
via Iron Oxide Catalyst	6
Glycerol	2
Hydrogen Cyanide	1
Isocyanates	10
Maleic Anhydride	7
Nylon 6	4
Nylon 6,6	3
Oxo Process	6
Phenol	8
Phthalic Anhydride via o-xylene	5
via naphthalene	3
Polyethylene (High Density)	5
Polyethylene (Low Density)	7
Polypropylene	7
Polystyrene	4
Polyvinyl Chloride	8
Styrene	7
Styrene - Butadiene Rubber	6
Vinyl Acetate via Acetylene	3
via Ethylene	1
Vinyl Chloride	8

INTRODUCTION TO APPENDIX IV AND V

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix IV discussion are:

1. Prediction of numbers of new plants.
2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix V discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX IV

Number of New Plants by 1980

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.
2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.
3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.
4. Estimate an economic plant or unit size on the basis of today's technology.
5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity		Capacity to be Added	Economic Plant Size	Number of New Units
				on-stream in 1980	Demand 1980			
Carbon Black	Furnace	4,000	0	4,000	4,500	1,000	90	11 - 12
	Channel	100	0	100	100	0	30	0
	Thermal	200	0	200	400	300	150	2

IV-2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It is felt that no useful end is served by creating a large number of sub-groupings because it will merely compound the problem of assigning a weighting factor. Therefore, it is proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x . However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

<u>Babcock</u>		<u>Walther</u>	
		<u>Primary</u>	<u>Secondary</u>
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it is proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	<u>Average</u>	<u>Rounded</u>
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____			
Process _____			
Increased Capacity _____			
Pollutant	Emissions, lbs./lb.	Increased Emissions lbs./Year	Weighting Factors
Hydrocarbons			80
Particulates			60
NO _x			40
SO _x			20
CO			1
Total			

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.
2. Approximately two orders of magnitude exist between top and bottom rankings.
3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane will be included.
4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.
5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.
6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. This determination is to be made on the basis of data reported on returned questionnaires.
2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.
3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.
4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It is proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

- (1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659
- (2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix V
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it is proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It is recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it is recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x . In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it is recommended that complete combustion be defined as the production of N_2 , thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors, as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:



Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:



Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices2. Significance of Emission Reduction Rating (SERR) (continued)

<u>Pollutant</u>	<u>Weighting Factor</u>	<u>Pounds in</u>		<u>Pounds out</u>	
		<u>Actual</u>	<u>Weighted</u>	<u>Actual</u>	<u>Weighted</u>
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO _x	40	0		1	40
SO _x	20	0		0	
CO	1	0	—	66.5	<u>66.5</u>
Total			8000		958.5

$$\text{SERR} = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

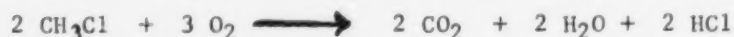
Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$\text{CCR} = \frac{342}{342} \times 100 = 100\%$$

and

$$\text{SERR} = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.



This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

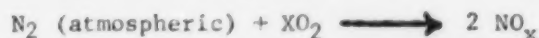
$$\text{SERR} = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)



Thus, $\text{CCR}_1 = 100\%$ and $\text{CCR}_2 = 100\%$ both by definition.

$$\text{However, } \text{SERR}_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$$

$$\text{and } \text{SERR}_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.
2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.
3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.
4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it is suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control DevicesOther Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 95\%$$

$$\begin{aligned} \text{and SERR} &= \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100 \\ &= \frac{6400 - 700}{6400} \times 100 = 89\% \end{aligned}$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\begin{aligned} \text{and SERR} &= \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100 \\ &= \frac{1000 - 180}{1000} \times 100 = 82\% \end{aligned}$$